EROSION-CORROSION BEHAVIOR OF DUPLEX STAINLESS STEEL UNS S32205 IN MINE ENVIRONMENT

by

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DISSERTATION

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February, 2019

DECLARATION

I hereby declare that the dissertation entitled “Erosion-corrosion behavior of duplex stainless steel UNS S32205 in mine environment” submitted for

MASTERS OF CHEMICAL ENGINEERING TECHNOLOGY

in the Faculty of Engineering and the Built Environment, University of Johannesburg is my original work. Any secondary information (either from a printed source or from the internet) has been carefully acknowledged and referenced. I further declare that this work has not been submitted before for any other degree in this institution or any other institution.

………………………………..   ……………………………..

Signature   Date

DEDICATION

This work is dedicated to my loving and supporting family who stood by me at all cost and most importantly my pillar, my Almighty God whom I drew strength from throughout the journey. I am grateful for all I have achieved and become so far.

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LIST OF JOURNAL ARTICLES AND CONFERENCE PRESENTATIONS

Journal Articles

[1] Moloto, A.K., **Seshweni, M.H.E.,** Mathe, N.J., Obadele, B.A., Aribo, S., Olubambi, P.A. and Ige, O.O., 2018. Influence of Shear Stress on Erosion–Corrosion of Stainless Steels in Simulated Mine Water. Journal of Bio-and Tribo-Corrosion, 4(2), p.26.

Conference Presentations

[2] Aribo, S., **Seshweni, M.,** Oluwafemi, S., Ogunbadejo, A., Ige, O. and Olubambi, P. (2018) Flow-induced corrosion behaviour of low alloy steel in the presence of mono-ethylene glycol. IOP Conf..Ser: Mater.Sci.Eng **430** (accepted for presentation at the Conference of the South African Advanced Materials Initiative)

[3] Aribo, S., Ojo S., **Seshweni M.,** Sanumi O., Ogunbadejo A., Ige O., and Olubambi P. (2018) Wear-corrosion behavior of 316L and API 5L X65 steels in inhibited 3.5wt.% NaCl environment-use of a designated tribometer
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ABSTRACT

The rotating cylinder electrode (RCE) is one rig constructed and designed to study the behaviour of the material under the effect of flow. The behaviour of hot and cold rolled UNS S32205 duplex stainless steel (DSS) in erosion-corrosion (EC) conditions were studied to monitor the material loss and surface degradation. The impact is highlighted and explained with the aim to offer better understanding regarding degradation phenomena. Mine water solution containing silica sand particles (SiO_2) was the environment of interest for this study. Both gravimetric and electrochemical methods (potentiodynamic polarisation (PP) and open circuit potential (OCP)) were adopted for the erosion-corrosion behaviour of the alloys. The cold rolled material displayed better resistance to erosion-corrosion at all speed tested in comparison with hot rolled material. The surface morphology for both materials revealed erosion dominating the erosion-corrosion process with minimal evidence of pitting. The hardness of cold rolled sample showed higher hardness as compared to hot rolled due to the impingement by sand particle hence better resistance to erosion-corrosion. The wear corrosion mechanism displayed grooving on the material surface especially at a higher speed. The effect of particles in wear mechanism play an important role. The electrochemical results showed increasing corrosion rate as the rotating speed of the electrode increased. The higher pH of mine water solution resulted in the passivation of the sample. The analysis trend was not surprising as the vulnerability of the surface layer increased with increasing velocity under the subjected conditions. Aggressive conditions and sand concentration are good enough to prove relation between wear rate and corrosion rate. The environmental impact was not aggressive enough to create much interferences hence the surface deterioration was not severe in all analysis.

Keywords: Corrosion, rotating cylinder electrode, stainless steel, mine water

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS

CNT	Centre of Nanoengineering and Tribocorrosion
TUT	Tshwane University of Technology
NRF	National Research Foundation
PTFE	Polytetrafluoroethylene
DSS	Duplex Stainless Steel
EC	Erosion Corrosion
RCE	Rotating Cylinder Electrode
PP	Potentiodynamic Polarisation
OCP	Open Circuit Potential
SEM	Scanning Electron Microscopy
OM	Optical Microscope
TML	Total Mass Loss
SiC	Silicon Carbide
µm	micro-meter
PSD	Particle Size Distribution
mm	millimeters
XRD	X-Ray Diffraction
EDM	Electronic Discharge Machine
WE	Working electrode
RE	Reference electrode
FESEM	Field Emission Scanning Electron Microscope
SCC	Stress Corrosion Cracking

PSD	Particle Size Distribution

CHAPTER ONE

1. INTRODUCTION

Erosion-corrosion (EC) is one of the material degradation processes observed in pumps and pipelines (Okonkwo and Mohamed, 2014), pipe bends and elbows (Khayatan et al., 2017), tube constructions, and other structures that alter flow direction or velocity (Islam and Farhat, 2017). Mining, chemical and petrochemicals industries, among others, experience erosion-corrosion problems as one of the predominant mechanisms in the degradation of these hydraulic systems. Such failure on the equipment results in non-functioning of the equipment reducing the design life period. The synergy between erosion and corrosion is still a subject of debate as the combined action of erosion and corrosion results in material degradation far more than the individual effect working separately (Aribo, 2014). Synergism between wear and corrosion also enhances rate of attack (Rajahram, 2010). Studies to achieve an understanding of erosion corrosion interaction was conducted in previous researches (López et al., 2016) and continuous to create a debate or bring a concern and great attention to researchers.

Slurry hydraulic systems are also vulnerable to the simultaneous attack of erosion and corrosion interaction with the environment. The material deteriorates gradually involving the electrochemical reaction or transfer of electrons through oxidation or loss of electrons to the environment or oxygen in the air. The basic electrochemical reaction during corrosion is when the metal being the anode balances the gain of electrons to the cathode. According to Rihan and Nešić, 2006 the generally accepted overall corrosion reaction in alkaline solutions is:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

Whereby Fe_3O_4 is usually found on the surface of the steel for protection in a de-oxygenated alkaline solution although there is a number of possible pathways.

To prevent premature failure, material developed with high corrosion resistance components or alloys against erosion and corrosion attack is necessary (Zheng et al., 2000). Duplex stainless steel (DSS) is one of the valuable strong material to the economy of most countries due to its low corrosion rate (Aribo, 2014). Moreover, DSS is known for its corrosion resistance, durability, good mechanical properties and manufacturing characteristics (Iversen & Leffler, 2010). They are reliable solution to slurry handling guaranteeing reasonable resistance to erosion corrosion attack. Manufacturing of such materials in industries differ according to the requirements and application of the material. Duplex stainless steel alternatively follows a manufacturing sequence of annealing for hot rolling and also to soften the material to facilitate cold rolling. Hot rolled formation is processed through rolling the steel at a high temperature making it easier to achieve the shape and form required (Pramanik et al., 2014).

Cold rolled steel is one of the dominant stainless steel product with variety of application such as chemical process industries (Iversen & Leffler, 2010). Cold rolling is usually performed after the intermediate annealing treatment. These types of formation can be applied to improve the strength characteristic of the material with good surface finish (Pramanik et al., 2014). Such impacts results in the gradual deterioration of the material during service. Fabrication of the material should be taken into consideration to avoid unexpected failure of the equipment. Materials such as duplex stainless steel are more recommended due to the combined properties of both ferrite and austenite.

Combination of ferrite and austenite in duplex stainless steels materials contributes towards the attractiveness of high corrosion resistance properties (Fargas et al., 2009). Their high corrosion resistance results in high demand application due to the aggressiveness of the environment in most industries, plants, mines, etc. Duplex stainless steel materials are mostly applicable on industrial equipment or engineering and petrochemical (Örnek and Engelberg, 2015; Fargas et al., 2009). Duplex stainless material can be used in pipe bends where most attack occur causing malfunctioning or even failure (Peng and Cao, 2016) especially in oil and gas industry.

Investigation of material's behavior assist in developing new material or improve the existing material properties for aggressive conditions. When the material is in contact with an aggressive environment the protective film on the surface is mechanically removed spontaneously and is difficult to repair (López et al., 2016). Hence, the reliability and the lifetime of the material in service is difficult to predict (Neville and Wang, 2009). Material development against erosion-corrosion is required which include material evaluation and design providing knowledge to a proper material selection. Equipment failure depends on the existence of the components in the environment which the material is exposed to. During corrosion the gain of electrons for basic electrochemical reaction pathway for alkaline environment take place as follows:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ ……………………………… (2)

Neutral or alkaline environment can be an aggressive environment impacted with solid particles impinging against the material surface. The encounter causes the material to wear while an electrochemical reaction takes place, causing corrosion (Rajahram et al., 2011, De Waard et al., 1991). Influences such as impact velocity, sand concentration and particle size (Wood et al., 2013) increase the synergy of erosion-corrosion damages on the exposed surface. In order to understand erosion-corrosion mechanism on the behavior of duplex grade materials in an aggressive environment that contains chloride ions and sulfide ions, research contribution to the development of the material is necessary. Improving the material properties for a corrosive environment minimize the impact of parameters on the performance of the material.

In the research of erosion-corrosion, different tests rigs have been used in the laboratories to conduct the experiments. The behavior of the material is tested to trace the cause and the type of the attack that occurred. Tests are also carried out to minimize the cost, consequences related to material degradation and to reach feasible decision in selecting an appropriate material. Identifying the attack assist in assessing its nature, mechanism and determine whether the design specification of the material conforms with the environmental specification for the material fabricated. The tests results performed in the laboratory for a specific environment should closely mimic the expected environmental results. For an instant, if erosion-corrosion mainly occurs due to the environment, the expected corrosion mechanism is expected to reflect in the laboratory tests. Tests are done using a specific test rig to obtain results and to assist in observing and understanding material failure.

Investigating the erosion-corrosion behaviour of a material assist in ascertaining its effectiveness and erosion-corrosion mechanism. Mining industries are looking for effective ways to combat material selection problem for erosion-corrosion environment. The correct use of effective methods to assess material selection for erosion-corrosion environment innovate ideas to reduce the cost of procurement of laboratory equipment.

Most laboratories find rotating cylinder electrode (RCE) convenient to carry out EC study tests which motivated this study. The immersion tests method of exposing the material to the environment of interest has to replicate the exact flow pattern in the field and must be reproducible. The immersion test quantifies the erosion-corrosion effect through appearance and mass loss.

1.1 Research Background

Material degradation occurs due to the different forms of corrosion that are involved. One of these is erosion-corrosion, which is of less focus in most research. Hence, investigating the behavior of duplex stainless steel in the mining environment is vital. Rihan and Nešić, 2006 explains the term erosion as a hydro-mechanical removal of the protective film by the flow while the main mode of metal loss is due to corrosion. Material attack due to this form of corrosion has been the most costly problem and often occurs in pumps and pipelines resulting in economic losses and methods of combating this corrosion are all expensive (Myles, 1995). The combined actions of erosion and corrosion have been one of the critical issues for contemporary research (More et al., 2017). Khayatan et al., 2017 reported some of the parameters, which are impact velocity, solid particle erosion and sand concentration.

These parameters limit the service life of the equipment (Rajahram et al., 2009; More et al., 2017), as well as playing a significant role in degrading the material during the erosion process (Rajahram et al., 2011). The degradation of the surface layer arises from mechanical and chemical reactions in contact with the aggressive environment especially containing solid particles. The mechanical reaction is when the layer of passive film on the steel is removed due to the harsh effects of a high-velocity or turbulent fluid (Kabeel and Abdelgaied, 2013). Whereas, the chemical reaction is when oxidation or an electrochemical reaction takes place on the metal surface due to air and moisture surrounding the material and the layer is removed (Wang et al., 2017; Rajahram et al., 2011).

1.2 Research Motivation

Duplex stainless steels have found preference in most industries and proved a successful choice due to their good corrosion resistance and higher strength. An unpredictable rate of erosion-corrosion in materials such as duplex stainless steel results in costly consequences due to failure attack. To develop a new material, testing is required to ascertain its effectiveness. Hence, laboratory tests to provide required information are done to aid in the proper material selection and to better understand the failure that occur in equipment.

The study of erosion-corrosion mechanism can be done through different methods. One of the most effective method is the use of Rotating Cylinder Electrode. Many tests performed in laboratories using duplex stainless steel proved this material to be appropriate for aggressive environment selection. However, particle shape, particle size, steel surface, environmental conditions, impact velocity, nature of the material and transporting medium (Okonkwo and Mohamed, 2014) can influence the steel pipelines degradation leading to failure. The degradation caused by the erosion-corrosion mechanism also depends on the nature of the material. The degradation rate experienced by components such as pumps, valves, tees and elbows in pipework is common for slurry flows (Neville and Hu, 2001). The geometry of the pipeline and erosion occurring during the slurry flow can be complex in pipe flow theory. Figure 1.1 represent the stagnant length of a normal impingement case.

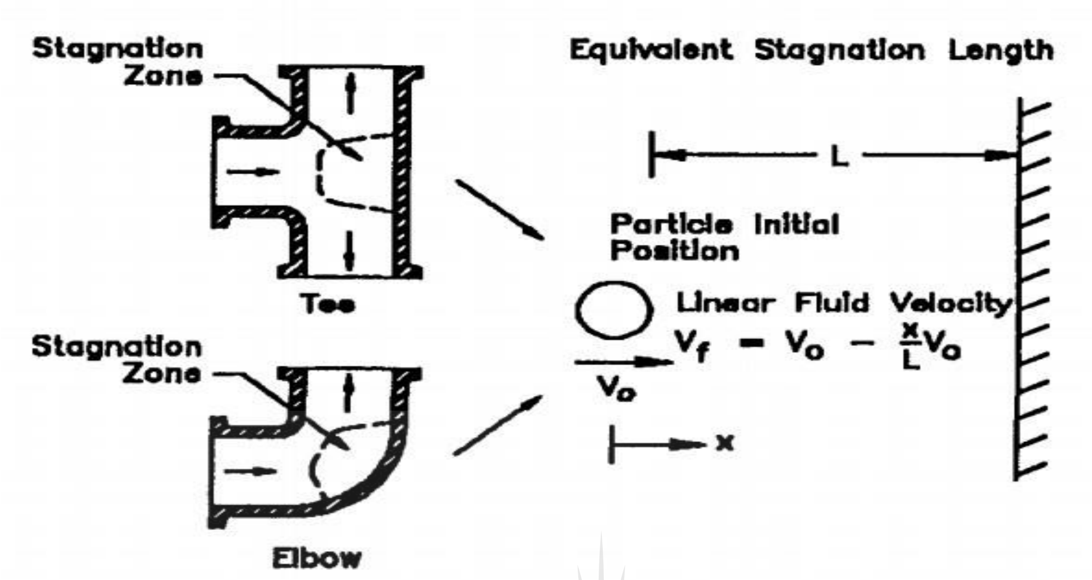


Figure 1.1: Equivalent stagnation length for a tee and an elbow (Shirazi et al., 1995)

1.3 Research Aim and Objectives

- The main aim of this project is to investigate the erosion-corrosion behavior of UNS S32205 cold and hot rolled duplex stainless steel in mine water using RCE erosion-corrosion test rig

Objectives of this study are to:

- Investigate the impact of variation of flow velocities (1000, 1500, 2000 and 2500 rpm) and particle concentration (5000 mg/l) on the material loss and surface damage
- Evaluate the surface degradation mechanism after the erosion-corrosion damage using SEM and Hardness Tester
- Correlate erosion-corrosion material loss and surface degradation of both alloys.

1.4 Justification for the Research

Standard type UNS S32205 cold and hot rolled steels are reported as very valuable grades with excellent performances of successful service applications experience (Verma et al., 2017). Laboratory tests are carried out as the most efficient way to investigate materials degradation. The laboratory experiment is done to observe the corrosion failure of the equipment in-service in mining industries to reflect the expected results in the industrial field or mimic what is happening in the industrial field through simulation. Factors such a pH levels and temperature are taken into consideration as this can be formulated on the basis of proper material selection. Therefore, further investigation on the material performance to reduce other industrial risks is necessary to limit the breakdown of pipeline system due to different parameters. Moreover, such investigation is to also improve the understanding of erosion-corrosion prediction in high pH environment.

1.5 Limitation of the Research

Limitation of the research depends on various factors such as unavailability of the consumables or dysfunctional equipment amongst others. The major hindrances to the research are malfunctioning software and the actual entrained particles in the gold mine to simulate the particle attack, hence silica sand has been adopted as the entrained particle in this experiment. Obtained data from the software together with the solid particles used as part of the experiment to achieve the aim and objectives of the research should offer evidence and quality of the work. Repeatability and reliability of the results or data should fairly serve the purpose of conducting the research. Failure to achieve such due to hindrances or errors jeopardise the quality of the work. To overcome the hindrances, since RCE or submerged impinging jet can replicate the experimental conditions to some extent, laboratory simulation is used impacted with the software. Higher sand concentration is also adopted to simulate a worst-case scenario that may not necessarily be possible in the actual field conditions. Room temperature has also been simulated for this work.

1.6 Scope of the Research

This research is limited to the use of standard duplex stainless steel UNS S32205 with two different processing histories - cold and hot rolled. The laboratory tests were performed correlating with the real time behavior of materials using the RCE corrosion test rig technique. The tests were done to accelerate the material degradation in short period of time to observe erosion-corrosion during in-service exposure. To achieve the aim and the objectives of the research experimental procedures were followed using a technique to investigate the material behavior in harsh conditions. The study was carried out with the use of rotating cylinder electrode (RCE) at rotating speeds of 1000, 1500, 2000 and 2500 rpm and a sand concentration of 5000 mg/L. Parameters were controlled carefully to observe the effect of varied velocity and sand concentration impact on erosion-corrosion of the metal and on corrosiveness of the environment. This was done to ensure reproducible results. Analysis were done before and after the experiment to observe the effect of erosion-corrosion behavior of the material in the exposed environment. Results were interpreted comparing the reference material (unexposed samples) surface with the ones undergone the test. Underground mine water from a gold mine in Mpumalanga province called Evander gold mine, South Africa, with a pH of 9.81 was adopted as the electrolyte while silica sand sourced from the University of Johannesburg, foundry laboratory was adopted as the erodent.

CHAPTER TWO

LITERATURE REVIEW

This chapter outline the material degradation or failure due to corrosion which is the most undesirable process as it effectively destroy metals especially when there is an interaction with the aggressive environment. The performance of the material depends on the alloying elements that form the material. The importance of material selection is also highlighted as there is a range of stainless steel material grades. Materials tend to mechanically and chemically deform due to the increasing anodic current density, passive film damage reactions, etc. Such reactions or causes of deformation are carefully outlined. To ascertain the effectiveness of a material subjected under corrosive environment, various methods are used. Advantages and disadvantages of these methods are carefully explained. Parameters affecting corrosion are also explained.

2.1 Introduction

Material performance investigation is oriented towards innovating developments to limit the effect of corrosion and prolonging the service-life of materials. Research has outlined various ways of material degradation occurring more rapidly due to the environmental conditions (Wood et al., 2013) and re-passivation is difficult under such conditions. Corrosive and erosive environments co-exist and can accelerate surface wear and material loss. Material failure is most undesirable as it effectively destroy metal or render the material useless (Myles, 1995). In industries such as paper, environment protection, fertilizer protection, food processing, chemicals production, Duplex Stainless Steel (DSS) has a wide application (Myles, 1995). Compared to other materials, DSS is also used on equipment such as pipes, pumps, agitators, valves and also in corrosive environments due to their mechanical strength, ductility and corrosion resistance, which can be experienced under severe conditions (Tavares et al., 2013). Material attack frequently occur on centrifugal pumps casing, eye of the impeller, pipeline accessories and hydraulic systems in most corrosive environment (López et al., 2016). In mining, pumps and pipes pump and transport corrosive fluid, which is the process water for leaching, mineral processes or chemical processes. Hossain, 2017 explains pipes as closed conduits that transport slurry under pressure in mining industry applications.

Pipes are easily attacked especially on the bends by corrosion when exposed to aggressive environments over a long period, increasing in roughness. With pumps as the flow progresses through the impeller passages, this interaction can lead to corrosion attack over a period. In mining, the composition of mine water (which could contain chloride) formed from the extraction or processing of minerals, depends on the mineral being mined. These media may contain solid particles that are erosive. Other industries that experience solid particle erosion of pipelines are petroleum industries during the transportation of oil and gas. Therefore, wear and corrosion acting in concert as shown in Figure 2.1 is greater than that from either process alone causing degradation process.

Figure 2.1: The macrographs of the erosion-corrosion mechanism on stainless steel (Bermúdez et al., 2005)

Pipelines exposed to environment such as CO_2 (carbon dioxide) and H_2S (hydrogen sulphide) also encounter erosion-corrosion in most industries and much effort has been put into studying these environments (Onyebuchi et al., 2017; Liu et al., 2017; Wang et al., 2017). Okonkwo and Mohamed (2014) also studied CO_2/H_2S environments during the transportation of oil and gas through steel pipelines. It was found that the solid particle erosion contained by the aggressive environment affected the pipelines resulting in erosion-corrosion. Corrosive ground waters containing high concentrations of chlorides and sulphates are also the main contributor coupled with high humidity resulting from the ambient temperature encountered underground in deep level mines (Myles, 1995). Wang et al., (2016) reported that corrosion failure still occurs during pipeline operation due to corrosive environments. The corrosive environment is mostly acidic and possibly basic or alkaline, resulting in the breakdown of the passive film (Wang et al., 2017).

Passive film resists degradation process to occur on the metal surface and once the passive film fails to protect the material, it then leads to de-passivation and subsequently corrosive attack (Wood et al., 2013). This film is easily penetrated by chlorides accelerating corrosion attack in acidic solution (Baboian, 2005). Moreover, the interaction of passive film, the microstructures, mechanical properties and the corrosion behaviour can be affected and influenced by the presence of hydrogen in the stainless steel (Luo et al., 2017). The performance of the material depends on the alloying elements that form the material. Alloying elements such as chromium, molybdenum, nitrogen and nickel offer duplex stainless steel a high corrosion resistance on the surface (Moura et al., 2008). Corrosion resistance on the surface can be enhanced again through a layer formed by a chromium-rich passivation (Shockley et al., 2017). The surface material with chromium content (Figure 2.2) provides the necessary protection decreasing the degradation process. Hence, duplex stainless steel is one of the quality material mostly in demand.

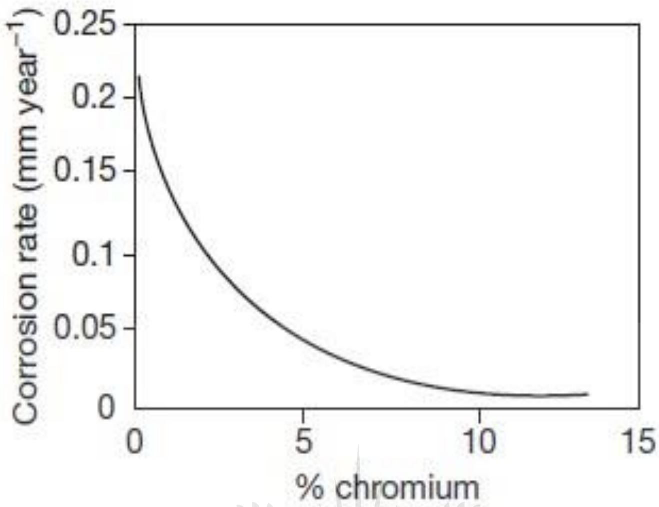


Figure 2.2: The effect of chromium content on passivity. Reproduced from Design Guidelines for the selection and use of stainless steel, specialty steel Industry of the United States, Washington, DC, USA (Iversen & Leffler, 2010).

2.2 Corrosion Attack in Gold Mines

Gold is a well-known raw ore in gold mines that is initially mined and processed separating it from other ores. It is commercially valuable and adds value to the business world. Gold undergoes a process called cyanide-leaching to extract gold from ore (Center, 2000). During leaching, gold is dissolved from the slurry and goes into the solution. These slurries travel through pipes and are propelled to the vats by pumps. Pipes and pumps are more sensitive to attack by abrasion and erosion than other units due to the high degree of turbulent flow they experience during handling of slurry (Carter 1986).

A number of mines including gold mine are extremely wet and corrosion has become a problem due to wet abrasion from dust residues that are constantly present on surfaces of piping and structures (Myles, 1995). Hence, the interaction of the corrosive environment with the metal results in gradual degradation of metals and alloys in many mining industries, which results in corrosion (Aribo, 2014). The solid particle erosion contained in the corrosive mining environment attacks the material by rubbing against the material surface (Pandya et al., 2017). Corrosion is a continuing problem and gold mine are among affected industries.

2.3 Mine Water Environment

Mine water simply refers to a process fluid, surface or groundwater present at the mine site. The quality of water used in mining industries has a great potential to affect the equipment in operation due to the sulphide that oxidizes from unmined ore causing the mine water to become aggressive (Winde et al., 2017). All metals are prone to corrosive attack if the environment is sufficiently aggressive (Myles, 1995). Steel is the most highly utilized metal alloy in mining water environment and its tendency to corrode in many environments is a disadvantage to the industry. In underground mines, there are SO_4^{2-} , Na^+, Ca^+, Mg^{2+} and Cl^- contained in the water with different pH values, create a corrosive environment (Hango et al., 2014). When a metal is exposed to an aqueous environment, uniform destruction of the material takes place. In slurry transportation systems, wear of piping and pipe-fittings is frequently a major problem (Myles, 1995). Where corrosive conditions are encountered, there are specific materials available for corrosive application and duplex stainless steel is among the best materials for such conditions.

2.4 Erosion-Corrosion

Erosion-corrosion is one form of severe type of corrosion on materials such as in pumps and pipes handling slurries (Giourntas et al., 2015). Material degradation depends on the interaction between the metal and industrial conditions. Research has been extensively done on minimizing and understanding erosion-corrosion but there are still incomplete understanding of the subject. Reports on the subject revolving around erosion-corrosion behaviour of hot and cold rolled duplex stainless steels is somehow still limited. Corrosion resistance in alkaline conditions varies depending on the kind of ions present, for example, chlorine dissolves the film leading to further corrosion (Myles, 1995). When designing a material for an aggressive environment, achieving the properties of a surface of a single material for that particular condition is technically and economically difficult to even good material such as duplex stainless steel, which becomes ineffective in the presence of solid particles (Shrestha, 2000). According to Rajahram et al., 2009, erosion-corrosion involves mechanical processes of solids particle erosion and electrochemical processes of corrosion (Figure 2.3).

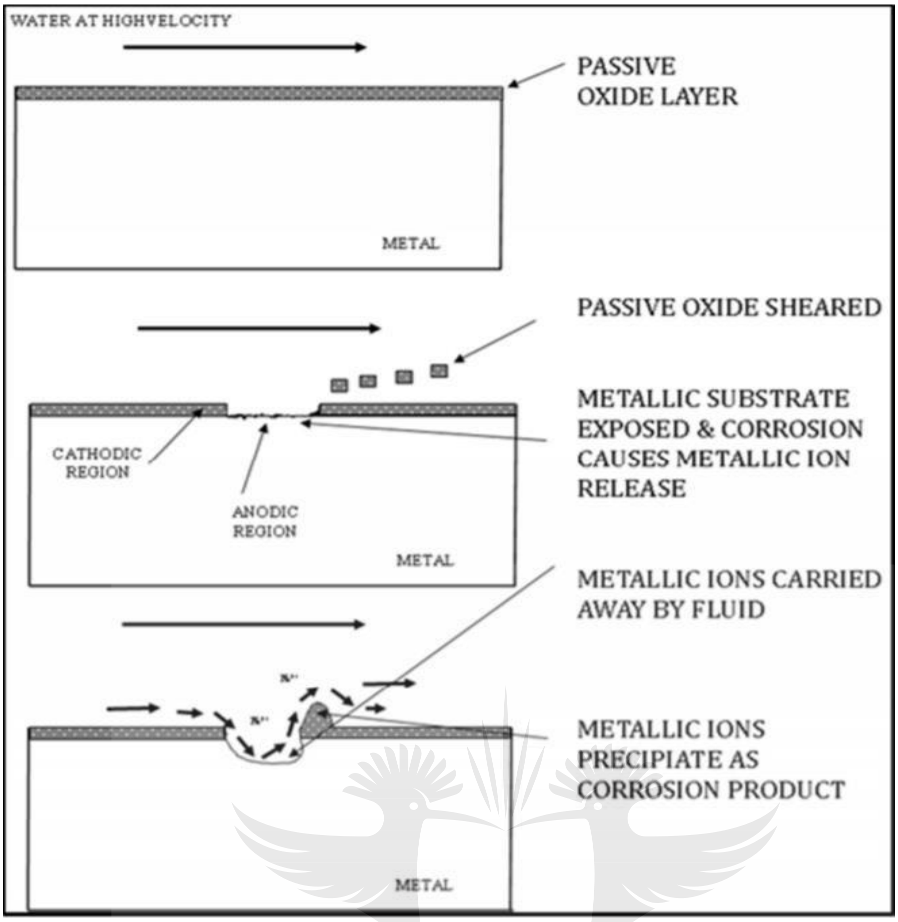


Figure 2.3: Steps involved during the erosion-corrosion process (Gall, 2013)

2.5 Material Selection

Understanding the mechanism of the erosion-corrosion behavior of a range of stainless steel material grades under these aggressive conditions (Giourntas et al., 2015) is essential. Due to corrosion phenomenon, the material developments to meet the practical industrial requirements are of urgent for high slurry erosion-corrosion environments. Corrosion devours corporate profits and eats up productivity at an alarming rate (Myles, 1995). Material design determines the reliability of the material in terms of industrial and economical aspect and the properties of the material, which are identified for a specific design. When the equipment is selected for an aggressive environmental purpose in mining, there are several factors to consider such as mechanical property, wear of the material, corrosion etc. A material alloy with more chromium improve the corrosion resistance of the material (Kimura et al., 2017). Studies done by Hango et al., 2014 revealed that corrosive mine water resulted in low corrosion rate of high chromium nickel based alloys at 6.8 pH compared to low chromium alloy.

Coating techniques on materials increase the initial cost therefore, most industries select the material due to its corrosion resistance (Giourntas et al., 2015). Proper selection of the material offers reliability and durability minimising the unexpected failure that can still occur reducing the service life of the equipment. Materials with low hardness and low wear resistance have a disadvantage of limited application in the industries (Li and Lei, 2017). Therefore, the process of material selection standardization for laboratory testing such as selection of suitable test rig for repeatable results to determine synergistic effect and the test rig will allow variation of parameters with good accuracy (Rajahram et al., 2009).

2.6 Pumps and Pipes

Industrial systems such as centrifugal steel pumps and steel pipes are most applicable in mining industries due to their reliability in transporting slurry and other process fluids. They usually operate under extreme pressures (Okonkwo et al., 2016) and proper selection of pumps and pipes material is required. Duplex stainless steel pipes and pumps are increasingly used for transportation of different types of fluids (Junior et al., 2017). Erosion resistance of materials depends on the hardness of alloys due to their strength to resist a permanent shape change. Failure arising in equipment performance gradually lead to unplanned shutdown. Corrosive environment contains severe ions such as chloride and sulphate, which increase the corrosion rate and reduce the performance of steel equipment (Bokati et al., 2017). Service life of this equipment depends on efficiency and resistance to the external interferences of the corrosive environment. Since 90's material alloy developments for corrosive environment and their application in industries such as oil has been promoted (Della et al., 2015). Such developments are necessary to minimize increasing economic loss.

(Hu and Neville, 2009) found it interesting to determine such critical conditions which move the damage mechanism from a flow-induced corrosion regime to erosion-corrosion regime. Premature failure in pipelines as shown in Figure 2.4 can be caused by the material processing steps, shape such as bend and elbows due to the sudden change in flow direction disturbing turbulent flow (De Waard et al., 1991; Mohammadi, 2011) leading to leakage.

Figure 2.4: Leaking pipes (De Waard et al., 1991).

2.7 Duplex Stainless Steel

Duplex stainless steel microstructures are a combination of good corrosion properties with interesting strength ratings. The microstructure of 2205 duplex stainless steel with 22 percent chromium consists of two principal phases of austenite (γ) and ferrite (α) with approximately equal parts (Luo et al., 2017). Austenite steels are most widely used grades known for their formability, more durable and excellent toughness. Ferrite steels consist of high chromium ranging from 10.5 to 27 percent (Charles, 2015) and are well known with their good ductility and not susceptible to stress corrosion. The combination of these two phases provide excellent corrosion resistance (Tański et al., 2014) and good strength as duplex stainless steel depends on its microstructure (Moura et al., 2008). The problem of erosion-corrosion has more impact regardless of the quality or the strength of the material. Hussain and Robinson (2007) performed tests on 2205 duplex stainless steel in simulated seawater containing sand. The mechanical deformation and an increase in erosion-corrosion rate influenced the increasing anodic current density and the damage of passive film through solid particles.

2.8 Passivity

Passivity occurs when a stable and tenacious passive film forms on the metal surface mitigating corrosion damage. Passive alloys exposed to the corrosive environment for a period of time exhibit passive film (Jiang et al., 2017) decreasing the corrosion rate. The film acts as a barrier between the material and the environment (Long et al., 2017), caused by insoluble corrosion products. The corrosion resistance of the material is illustrated in Figure 2.5 below.

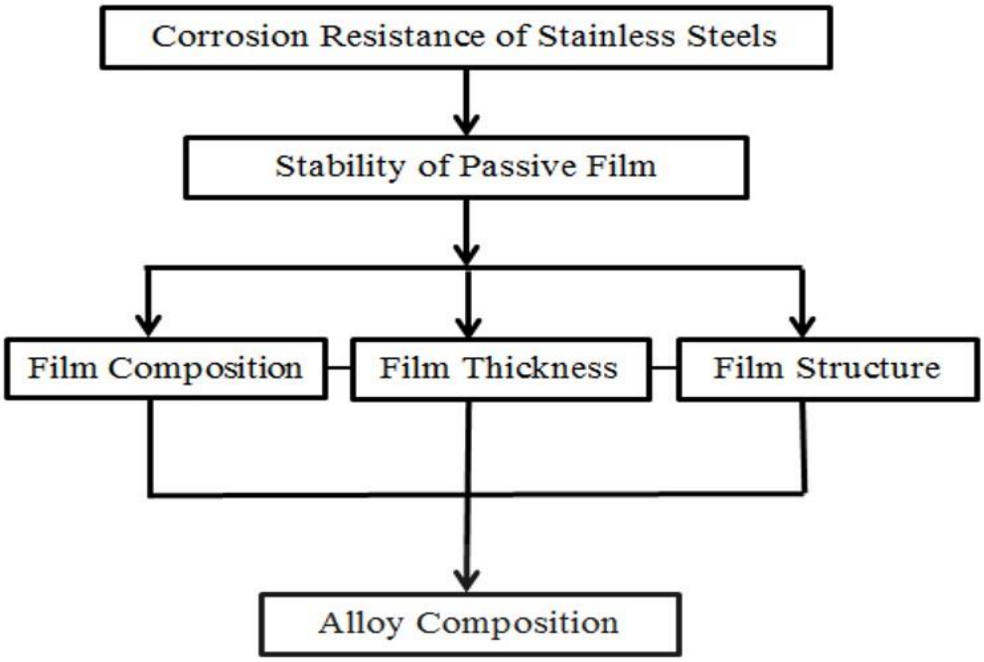


Figure 2.5: Corrosion resistance of stainless steels and passive film properties relationship (Qiu, 2002)

Stainless steels have high resistance to corrosion due to passivity in aggressive environments. During passivity, there is a drastic decrease in corrosion rate whereby the metal becomes less affected by the environment due to the loss of electrochemical reactivity. Figure 2.6 illustrates the three effects of passivity on the material. Active region is the region where anodic dissolution is high and the alloy behaves like active alloy on the metal hence the behaviour is the same as the normal metal. When the corrosion rate starts to increase due to an oxidising agent the passive region will start. Increase in corrosion rate due to, for instant high concentration of acid, proceeds to transpassive region.

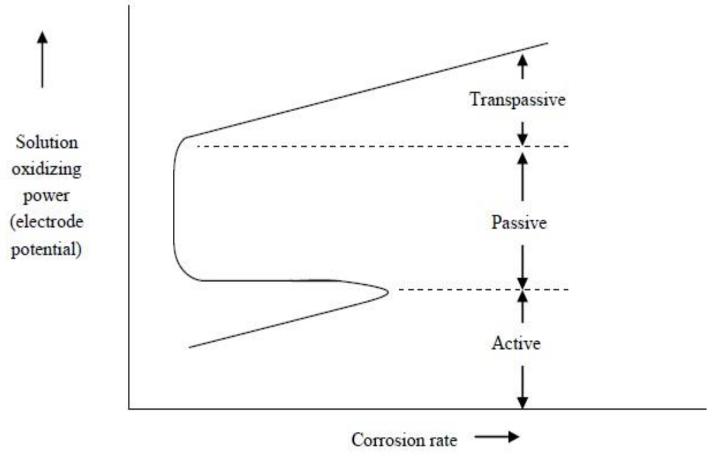


Figure 2.6: Corrosion characteristics of an active metal (Nelwalani, 2014)

Passive film is beneficial to increasing synergistic corrosion rate in protecting the material. Erosion-corrosion depends on the environment containing high concentration of acids placing the exposed material at risk. A study by Wang et al., 2016 showed an erosion-corrosion phenomenon occurring on a natural gas pipeline of 2205 duplex stainless steel in a wet gas environment. The acidic gas contained agents such as CO_2, H_2S and Cl^- transported through the pipeline resulted in increasing corrosion rate at accelerating velocity with high relative humidity.

2.9 Electrochemical Reaction

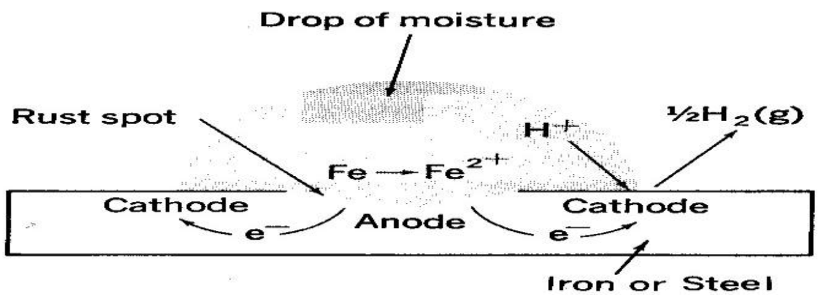


Figure 2.7: Typical formation of corrosion on iron or steel.

The mechanism occurring on the material surface as a result of a corrosion process in an aqueous solution is electrochemical reaction. Corrosion involves electrochemical whereby anodic and cathodic reaction (Figure 2.7) play a role in the oxidation and reduction of a metal. During anodic reaction, electrons are lost by flowing to the cathode sites where they are consumed, that is, oxidation. Cathodic reaction is when electrons are being gained and that is referred to as reduction. The positive current flow is released from the anodic site to the cathodic sites. In the context of corrosion potential and current are often mentioned. Potential, also known as voltage, can be explained as the difference between the metal and the electrolyte measured across the metal electrolyte interface (Nelwalani, 2014). The rate at which anodic and cathodic reaction exchange electrons is called corrosion current.

2.10 Electrochemical Principles

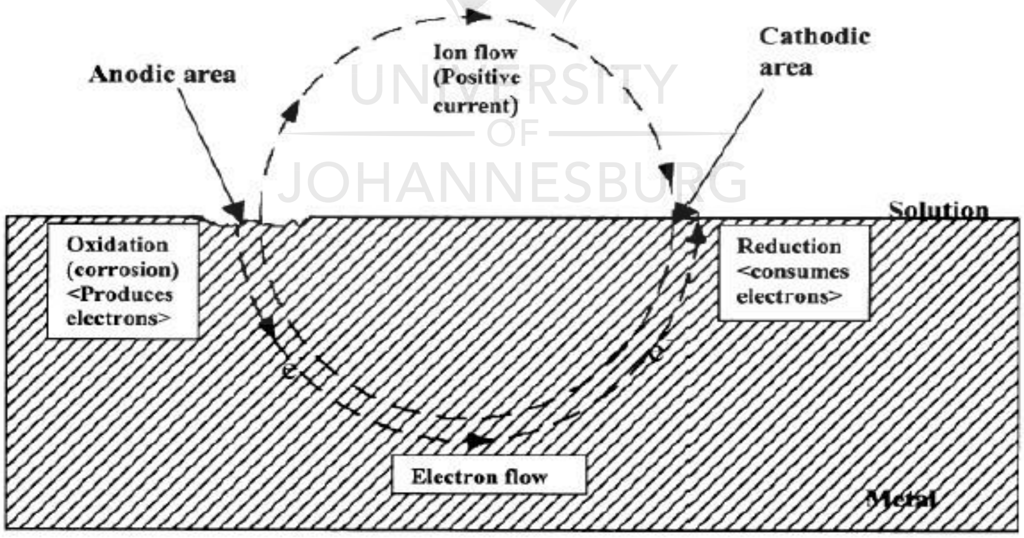


Figure 2.8: Schematic diagram for metal corroding in an acid (Nelwalani, 2014)

During the transportation of fluid and gases especially containing acids, the material life service is shortened incase the material surface has low corrosion resistant damaging the surface of the pipeline and pumps. As a result, the electrochemical reaction governed by both anodic and cathodic reaction occur. Figure 2.8 shows a metal that is exposed to an acidic condition whereby anodic area is experiencing oxidation, which is the loss of electrons, through the metal flowing to the cathodic area where electrons are consumed. Current flow is in a clockwise direction (or positive) from the anode area through the electrolyte to the cathode area directly opposite to the flow of electrons which is anticlockwise (or negative) (Nelwalani, 2014).

2.11 Electrochemical Methods

There are various methods to study erosion-corrosion and the alternative method is by electrochemical methods (Rajahram et al., 2011). Erosion-corrosion tests done in the laboratory by simulation often do not reflect exactly the reality happening in the industry. However, different electrochemical methods are used to understand the synergism of erosion-corrosion. Pipe Flow Loop, Rotating Cylinder Electrode, Slurry Pot Erosion Tester, Jet Impingement Rig, Electrochemical Noise Measurement, Rotating disk and Coriolis Erosion Tester are popular methods reported when studying erosion-corrosion properties.

Rajahram et al., 2011 mentioned some of the importance of electrochemical methods when researching corrosion and its mechanism on the material due to environmental conditions

- The methods provide quantitative and qualitative information and estimate the rate of erosion-corrosion of service equipment
- They assume the service life of the material of interest
- Allowing the engineer to plan ahead for replacement of parts as deemed necessary, for protection required and necessary maintenance

- The advantages of using this method are that the information is in real time when recording corrosion reactions as they occur on the surface

2.11.1 Pipe Flow Loop

Rajahram (2010) explained pipe flow loop as one type of experimental technique that is able to predict erosion-corrosion on actual pipe geometries. To construct this type of equipment is costlier hence; it is rarely used in most laboratories. Pipelines transporting slurries are affected at the bends, tees and elbows by the corrosive environment increasing corrosion rate. Laboratory simulations of erosion-corrosion tests are based on what is taking place in the industries. With pipe flow loop experiment, loops are scaled down to the size of the laboratory and accurate assumptions are made on field flow. The flow loop has a tank to contain the slurry that is continuously stirred. The slurry is recirculated from tank to the loop then back to the tank by a pump. To calculate the eroding rate using this technique the actual pipe thickness is used. Advantages, disadvantages and application of pipe flow loop are mentioned below.

Advantages of Pipe Flow Loop

- Developments for pipe flow loop are mathematical expressions for velocity profiles, mass transfer characteristics and current distribution
- Shear stress is constant over the electrode surface at fully developed flow if the coupon does not destruct the flow pattern
- The study of differential stress can be possible if the placement of coupons is parallel and perpendicular to the flow field

Disadvantages of Pipe Flow Loop

- Interpretation of results may be unclear by non-uniform mass transfer.
- The system invites entrainment of particles and/or air bubbles that may not be desirable.
- These systems are expensive and difficult to operate. Unreliable challenges may minimize collection of long-term data
- The use of pumps is part of the setup in pipe flow loop operation and may create mechanical problems of oxygen leakage into the system but can be avoided by using a magnetic drive pump.
- When flammable, toxic, corrosive fluids are used there are possibilities of spills or floods with the use of pipe flow loop for handling them

Applications

The flow loop can be used to determine whether a given reaction is influenced by mass transport limitations, but the non-uniform mass transfer associated with the system hampers this application. The flow-loop system can be used to study the effects of oxygenation or differential mass-transfer cells.

2.11.2 Rotating Cylinder Electrode

The RCE technique (Rajahram et al., 2009) which is simple and easy to implement, can investigate the corrosive process of the fluid passing through the sample surface by electrochemical techniques.

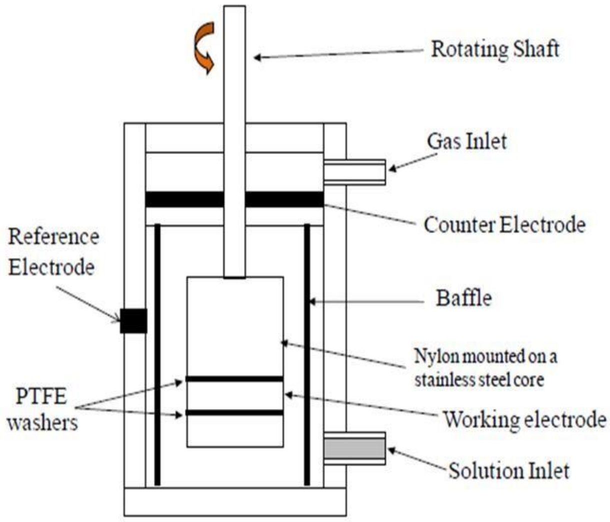


Figure 2.9: Schematic diagram of Rotating Cylinder Electrode (Rajahram et al., 2011)

Advantages of Rotating Cylinder Electrode

- Hydrodynamic flow is well defined. Empirical correlations are used to obtain mass-transfer coefficients and friction factors in turbulent flow.
- Both the current and potential distributions are constant if the electrode, which can be modeled easily, is usual to all electrically isolating planes
- The system is easy to use. No pumps are needed since the flow pattern is induced by the rotation of the cylinder.
- Only standard machining is needed to fabricate the electrodes.
- The system is adaptable to many solutions and hydrodynamic environments.

Disadvantages of Rotating Cylinder Electrode

(State-of-the-Art Report on Controlled-Flow Laboratory Corrosion Tests, 1995)

- The impact angle cannot be controlled due to its rotational flow field

- If the electrode is unusual to all electrically isolating planes, the current and potential distributions will not be constant at once. Such non-uniformity makes interpretation of results dependent upon application of sophisticated mathematical models.
- Once encased in the electrically isolating epoxy or PTFE, the electrode surface can be difficult to polish.
- Maintaining low-resistance electrical connection to the rotating electrode can be difficult.
- As for all systems using rotating coupons, a bearing guided shaft is needed to avoid wobble.

Applications

The rotating cylinder can be used to determine whether a given reaction is influenced by mass transport limitations in a turbulent-flow regime. It is used to measure mass transfer-limited currents and, since correlations are available, these measurements can be used to determine the diffusivity of the limiting reactant (Rajahram et al., 2009).

A research by Ige et al., 2017 was conducted on erosion-corrosion behaviour of spark plasma sintered WC - 12Co in aggressive media using rotating cylinder electrode. Corrosion and hardness tests were carried out together with the surface morphology examination. Results showed total mass loss resulting from corrosion revealing least degradation resistance in sulphuric acid as compared to simulated environment. Mine water and seawater were the simulated solutions of with and without sand particles environment. Results further showed protective film forming in both environment of with and without sand particles during cyclic potentiodynamic polarization.

2.11.3 Slurry Pot Erosion Tester

A slurry pot erosion tester is a well-established technique for studying pipeline transportation of slurry. In previous research a slurry pot erosion tester was used and modified as the test apparatus (Rajahram et al., 2009) for erosion-corrosion studies

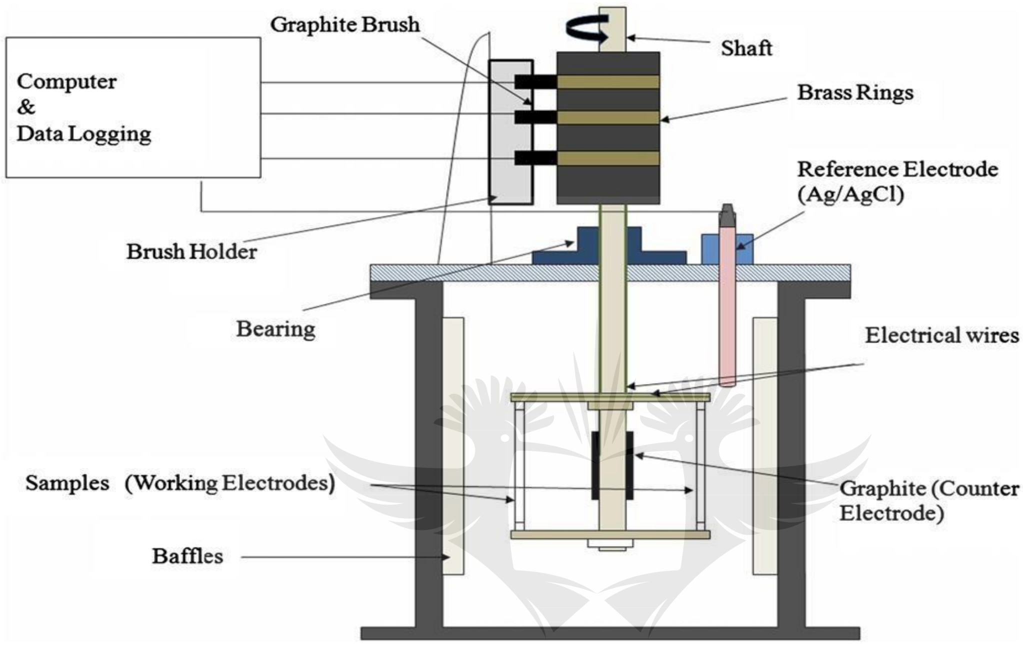


Figure 2.10: Modified slurry pot erosion tester to perform in-situ electrochemical investigation (Rajahram et al., 2009).

Advantages of Slurry Pot Erosion Tester

- The speed of the motor is controlled by adjusting the frequency of the variable speed drive
- The slurry and the erodent (silica sand) which are contained within the pot can be handled easily
- Results are repeatable and reproducible with low errors
- It allows good control of test parameters besides its relative ease of usage and cleaning

- The rotational flow of the slurry in the pot also allows multiple impact angles to be achieved at the same time in this rig.
- Provide invaluable information on the understanding of erosion.

Disadvantages of Slurry Pot Erosion Tester

- The impact angles of the erodent cannot be controlled due to the rotating flow field of the slurry
- The cylindrical sample geometry also makes the polishing of the test sample difficult
- The limitations of using this test rig is due to cylindrical test samples that are difficult to polish by conventional flat wheel polishing method.

A research on three target materials of stainless steel (SS316L/UNS S31603), carbon steel (AISI 1020/UNSG10200) and nickel-aluminium bronze (NAB/UNS C63200 to investigate the role of parameters influencing erosion-corrosion with the use of slurry pot erosion tester was conducted. Parameters involved erodent size, erodent concentration, flow velocity at varied test conditions of 3.5% NaCl and 0.3 M HCl to reveal the effect on erosion-corrosion. According to the results obtained SEM showed similar EC mechanism of SS316L and NAB whereas AISI showed dominant influence of corrosion mechanism on the material. Materials were also compared based on EC, SS316L showed lowest EC mass loss rates in all test conditions followed by NAB then lastly AISI. For the combined action of erosion and corrosion, NAB showed the best resistance to the synergy with highest negative synergy value. These proves that erosion-corrosion can be severe based on the material components under the influence of an aggressive condition containing solid particles.

2.11.4 Jet Impingement Rig

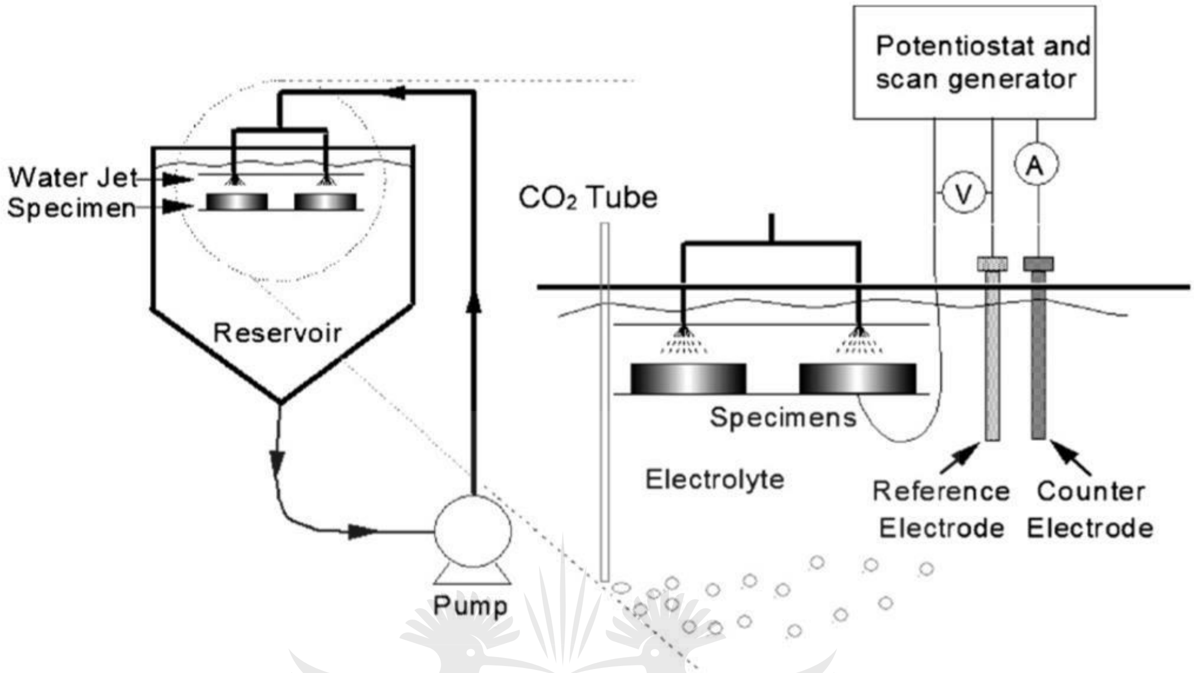


Figure 2.11: Schematic diagram of the submerged impinging jet (Neville & Wang, 2009.)

Advantages

- The characterization of the fluid flow is good and the hydrodynamic shear is a linear function and can be determined indirectly for measurement of mass-transfer-limited currents.
- If the entire disk lies within the stagnation region, the mass transfer to the disk becomes uniform. This uniformity prevents establishment of differential oxygenation cells and aids in the interpretation of experimental results.
- The electrode is both stable and flat allowing the use of in-situ determination of film thickness by ellipsometry.

- Shear-induced erosion-corrosion is studied with fewer experiments than with rotating electrodes.

Disadvantages

- Uniform mass-transfer characteristics are observed only in the stagnation region for impingement normal to the flow. These characteristics are not observed for other impingement angles or outside the stagnation region.
- The impinging-jet setup uses a pump in its operation.
- The system invites entrainment of particles and/or air bubbles that may not be desirable.

- For cases in which mass transfer limits corrosion, the mass-transfer-limited current distribution is not necessarily uniform. Indeed, the primary distribution (seen when the ohmic resistance of the solution controls the current) leads to an infinite current at the periphery of the disk.

Applications

The flow is well defined as long as the nozzle is between 5 and 10 nozzle diameters away from the electrode. Impinging-jet electrodes can be used in a manner similar to that of the rotating disk electrode if the electrode diameter is less than or equal to the diameter of the jet nozzle. In this configuration, the electrode lies entirely within the stagnation region where mass transfer is uniform. The system can therefore be used to determine whether a given reaction is influenced by mass-transport limitations. By use of segmented electrodes or post exposure examination of the electrode surface, the impinging-jet system can be used to study the effects of oxygenation or differential mass-transfer cells if the electrode diameter is more than five times larger than the diameter of the jet nozzle. The design of the flow system follows that of the flow-loop systems described in the following section.

2.11.5 Electrochemical Noise Measurement

The fluctuations that are generated in current or potential from a freely corroding surface material can be used to characterize the electrochemical phenomena. This is referred as electrochemical noise which provides information on the passive film breakdown. According to Rajahram et al., 2011 electrochemical current or potential measurement is plotted as a function of time in which the frequency, data acquisition sampling rate and test duration can be varied. Data from electrochemical noise can be analysed in terms of the size, shape and distribution of the potential or current transients.

2.11.6 Rotating Disk

Advantages

- Hydrodynamic flow is well characterized. Mathematical models for current and potential distribution developments are available in the open literature.
- The system is easy to use. No pumps are needed since the flow pattern is induced by the rotation of the disk
- Only standard machining is required to fabricate the electrodes and, once encased in the electrically isolating epoxy or PTFE, the surface is easily polished and is therefore reproducible.
- The system is easily adaptable to many solutions and hydrodynamic environments.
- Both electrochemical methods and mass loss can be used to provide information on corrosion rates.

Disadvantages

- The current and potential distributions are not uniform at the same time. As a result, interpretation of data obtained below the mass-transfer-limited current requires application of sophisticated mathematical models.
- Even at high rotation speeds, a portion of the disk operates under laminar flow, whereas most industrial systems operate under turbulent flow. The non-uniform flow regime seen at high rotation speeds can result in potentially misleading differential mass transfer effects. • Maintaining low-resistance electrical connection to the rotating electrode can be difficult.
- As for all systems using rotating coupons, a bearing guided shaft is needed to avoid wobble.

Applications

The rotating disk can be used to determine whether a given reaction is influenced by masstransport limitations. It is used to measure mass-transfer-limited currents and, since an explicit mathematical relationship is available, these measurements can be used to determine the diffusivity of the limiting reactant.

2.11.7 Coriolis Erosion Tester

A coriolis erosion tester consist of a rotor which fits two specimen holders on each side. To pass slurry across the test surface coriolis erosion tester uses a combination of centrifugal and coriolis acceleration in a rotating rotor. As the rotor is rotating, erodent impinging against the test surface is channeled from the slurry inlet pot from the central chamber outwards. These causes wear erosion due to the erodent moving against the surface. The advantage of using this type of tester is that the mixture of elastic and plastic deformation that occurs during the test simulates industrial equipment quite well. This rig is dominated by erosion at low impact angle.

2.12 Research Parameters

2.12.1 Effect of Flow

Turbulence flow gives rise to cavitation erosion because of cavities being formed within the liquid. The influence of fluid flow rate on corrosion is dependent on the alloy, fluid constituents, fluid physical properties, geometry and corrosion mechanism (Baboian 2005). In full-flow slurry conditions wear is frequently reported due to erosion only whereas, for carbon steel, the wear mechanism is usually a mixture of corrosion, erosion, and some synergistic effect between the two (Myles 1995). High corrosion rate rises from a damage by high flow velocity. The study on the effect of hot caustic, NaOH solution, was done on mild steel for EC test by Rihan and Nešić (2006). High-pressure/high-temperature nickel flow loop was constructed to carry out the experiment.

The effect of the flow on the rate of EC of 1020 steel in 2.75 M NaOH solution at a temperature of 160 ^{0}C and velocities of 0.32 and 2.5 m/s was conducted (Rihan and Nešić, 2006). Weight loss and SEM were among other electrochemical methods used. Eight electrodes were used to monitor the loss rate whereby four were placed at the low velocity section, while the other four were placed in the high velocity section. Results showed that the corrosion rate of the coupons in the high velocity section was generally higher than that of the coupons in the low velocity section. The coupons were placed in different flow, the disturbed flow region and the fully developed flow region.

2.12.2 Slurry

The slurry erosion corrosion parameter is often a concern in a mining industry among others due to the solid particles which are erosive. These erosive environments damage the slurry handling components such as pumps and surfaces of the impellers and walls of the pipelines and resulting in wear impact (Zheng et al., 2000). Under these conditions, a combined action of erosion and corrosion takes place at the same time. Rajahram et al., 2011 investigated the effect of velocity, sand size and sand concentration on a passive metal. Samples were subjected to a set of erosion-corrosion experiments. This was done to understand the erosion-corrosion process. The results showed an increasing velocity and sand concentration increasing the current levels during erosion-corrosion. However, an increasing sand size had a more complex response.

Table 1: Factors Influencing Erosion (Rajaram, 2010)

Erodent characterisation	**Material**	**Fluid characteristics**	**Flow condition**
Hardness	Hardness	Viscocity	Fluid velocity
Size	Fracture toughness	Temperature	Impact angle
Shape	Ductility	Density	Flow trajectory
Mass	Surface roughness		Particle interactions
Concentration	Microstructure		

2.12.3 Solid Particles

Solid particles are common in the mining environment as they are part of the slurry during processing of ores such as gold. Particles influence erosion as they impinge on the target material depending on their size, shape, mass and concentration. Previous studies have shown that introduction of erosive particles turns the surface more active, shifts the corrosion potential to lower values and promotes an increase of current densities, in comparison with the results obtained without particles (López et al., 2016). Figure 2.12 shows that the particle size could have more effect on the material, increasing the corrosion rate on the metal. Damage caused by suspended and/or entrained solid particles in mining and metallurgy industry require significant attention amongst researchers in recent years (Lindgren & Perolainen, 2014). Determining the corrosion current density by potentiodynamic polarization is the most direct way to determine the corrosion rate (Hu and Neville, 2005).

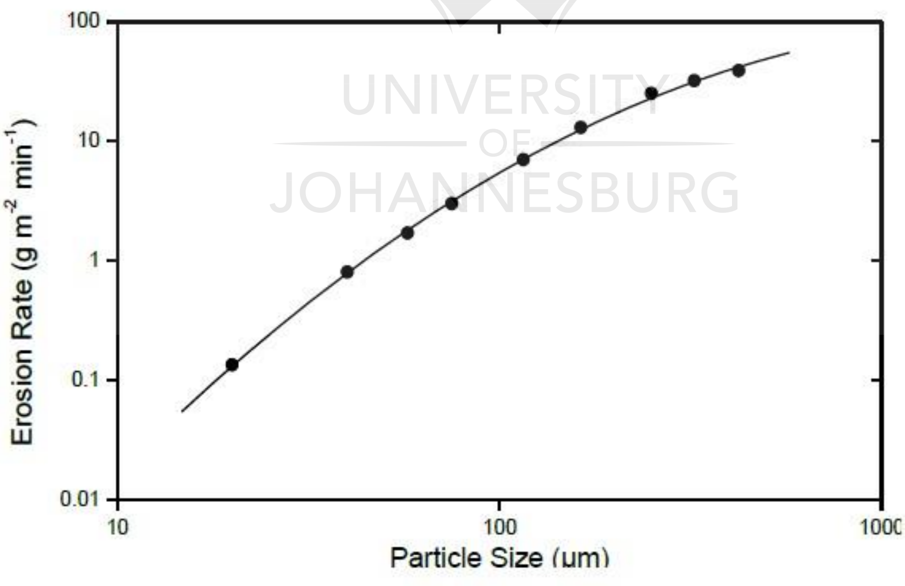


Figure 2.12: Impact of particle size vs erosion rate (Rajahram, 2010).

Hussain and Robinson (2007) researched on erosion–corrosion of 2205 duplex stainless steel to show the effect of sand particles in an aggressive condition of flowing seawater.

Results showed that the particle impacted the surface and eroded the oxide in seawater environment. Erosion-corrosion of 2205 DSS material tested using Jet Impingement apparatus was measured through electrochemical polarization performed. The obtained erosion-corrosion measurements results of the material was through an increase in anodic current density that occurred when the passive film was damaged by particle impacts. The difference between Hussain and Robinson (2007) research study with this study is the environmental conditions the materials are exposed to.

2.12.4 Weight Loss

When the material is exposed to the corrosive environment to determine the corrosion rate of the material the weight or mass loss can be calculated. Weight loss is due to electrochemical corrosion. The synergy effect of erosion and corrosion is more severe to materials resulting in weight loss which is one of the corrosion products (De la Fuente et al., 2011). According to Zheng et al., 2000 who studied the appropriate way of developing materials for aggressive slurry flows found a decrease in weight loss due to electrochemical corrosion as Naz et al., 2017 also discovered, on the steel material in aggressive environment. This is due to the synergistic effects of erosion and corrosion which can be optimized to develop the material for slurry erosion-corrosion resistance. Synergy simply explain the combined action of erosion and corrosion. According to Rajahram et al., 2009 synergism is the difference between the combined erosion-corrosion wear rate and the sum of pure erosion and pure corrosion acting separately and can be expressed by

$S = T - (E + C)$ ……………………………………………….(3)

S- Additional wear rate due to the synergistic interaction between erosion and corrosion, T- Total wear rate due to erosion-corrosion, E- Wear rate due to pure erosion, C- Wear rate due to flow corrosion

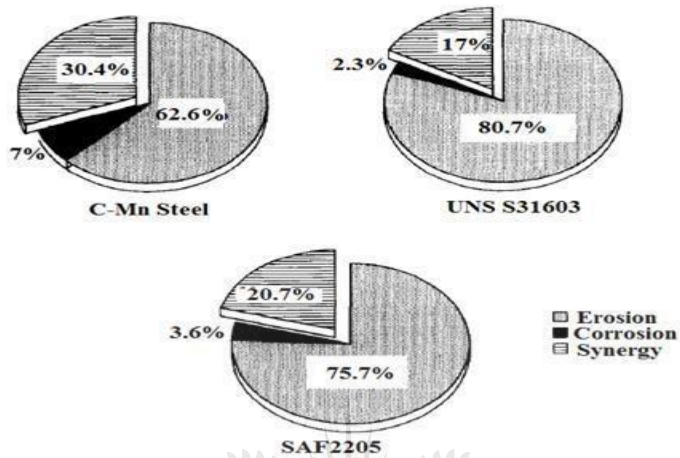


Figure 2.13: Breakdown of total weight loss under erosion-corrosion at 50^{o}C (Neville et al., 1995.)

2.13 Erosion Enhance Corrosion

Erosion-corrosion is complex and adversely affecting pipelines by the influence of different parameters and environmental conditions. A metal exposed to an aggressive environment with solid particle becomes vulnerable to the synergistic attack. This is due to the interaction of erosion with corrosion which is mechanical and electrochemical effect having impact and resulting in mass loss (Guanghong et al., 2010). The presence of solids induce erosion and interact with corrosion resulting in material degradation mechanism (Hu and Neville, 2009). The solid particles could be through processes such as leaching. Erosion of surface by stream of solid particles has been an issue of concern for decades and could involve weight loss and surface microstructure (Okonkwo and Mohamed, 2014). In such processes erosion which is mechanical affect or enhance corrosion through electrochemical reaction. The pipeline flow of slurry due to kinetic energy enable the particles to travel at a certain speed. Surface material can be affected by particles with different sizes and shapes and aggressiveness of the environment. Mining equipment most possibly obtain damage on the surface layer which is more affected by erosion and mechanical damage rather than corrosion (De Waard et al., 1991). Solid content dominates on the severity of erosion.

2.14 Corrosion Enhance Erosion

Corrosion take place when the surface material degrades due to chemical reaction. The reason why the study is more focused on erosion corrosion is mainly because this form of corrosion is recognized as a critical one for the industry. Previous studies provided clear evidence of complex corrosion behavior through morphology or mechanism (Wood et al., 2013, Rajahram et al., 2009 and Shockley et al., 2017). It could assist in obtaining how fast steel can corrode. Corrosion rate indicate the behavior of the material and if the material is suitable for intended use. Corrosion products such as rust and mass loss which may increase further due to build-up have undesirable effects and are evidence to material surface degradation. Increase in corrosion rate become more influenced depending on the affecting parameters. Corrosion enhance erosion in more complex processes through roughening of the metal influenced by the impact angle of the solid particles (Okonkwo and Mohamed., 2014) in most slurries.

2.15 Literature Summary

The reason for this study is based on the material attack due to erosion-corrosion often occurring at different areas of different equipment with the possibility of removing the protective surface films partially or completely overtime, thus causing severe subsequent failure. This work is necessary in conducting laboratory work on standard type UNS S32205 cold and hot rolled steels as are reported as very valuable grades with excellent performances of successful service applications experience (Verma et al., 2017). Laboratory simulation such as the use of RCE can replicate industrial conditions to some extent. Though it is difficult to use the actual entrained particles in industries such as gold mine to simulate the particle attack, silica sand has been adopted as the entrained particle in this experiment. Higher sand concentration is adopted to simulate a worst-case scenario that may not necessarily be possible in the actual field conditions. Room temperature has also been simulated for this work. This is done to assist bridge some of the gaps on the challenges faced with material selection in the mining environment and erosion-corrosion attack affecting the steel alloys used in mining industries among others. The need for laboratory experiments are important in assessing the effectiveness of the material, assume the service life of the material of interest and also assist with the rate at which the corrosion damage occurred. Hence the test method to assess material selection is necessary to be repeatable and reproducible to solve the economic issue with the equipment to be considered.

CHAPTER THREE

METHODOLOGY

3.1 Introduction

This chapter outline the approach taken in the laboratory during erosion-corrosion tests using Rotating Cylinder Electrode. To quantify the erosion-corrosion damage, proper sample preparation using metallographic steps of grinding was carefully followed, image analysis of experimental materials using Zeiss Axio Observer optical microscope and Carl Zeiss Sigma Field Emission Scanning Electron Microscope before and after the experiment were obtained for the surface morphology. Future-Tech FM 800 microhardness testing machine was employed before and after the erosion-corrosion tests to evaluate the hardness of the material. The electrochemical techniques were also done for Open Circuit Potential and Potentiodynamic Polarization to determine the corrosion behaviour of the alloys.

3.2 Methodology Flow Diagram

In achieving the aim and the objectives of this research study, the procedure was done as follows:

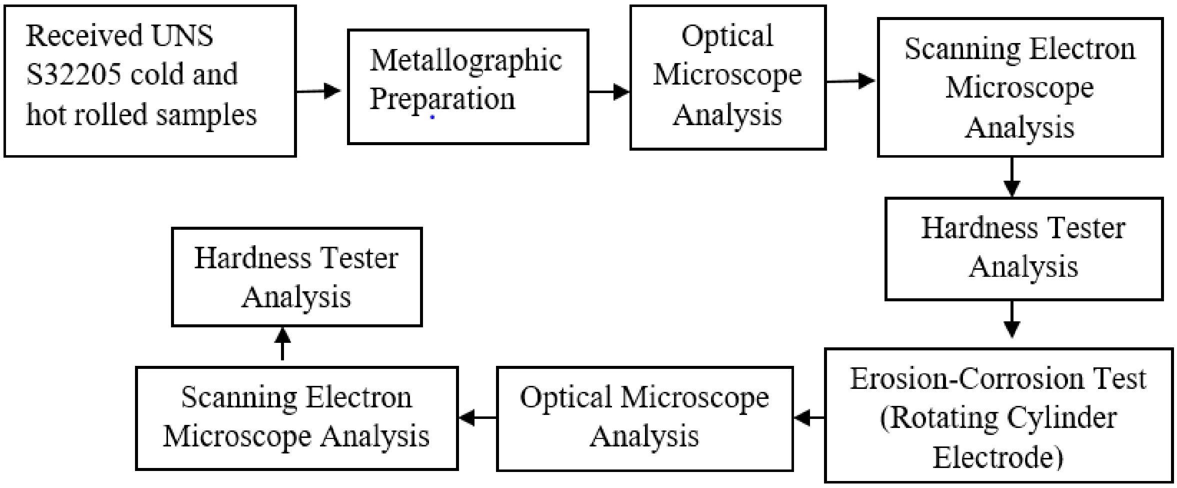


Figure 3.1: Methodology Flow Diagram

3.3 Sample Preparation

3.3.1 Cutting

Material of UNS S32205 cold and hot rolled sheet plates obtained from Columbus Stainless (Pty) Ltd, Mpumalanga, South Africa with chemical composition presented in Table 2 were taken for cutting. To avoid mechanical damage, correct cutting method of wire cutting using wire Electronic Discharge Machine (EDM) was done according to the sample geometry required for the RCE equipment. Samples were cut in cylindrical shape (Figure 3.2) with inside and outside diameter of 9.6 mm and 15 mm respectively, the thickness was 6.2 mm and the exposed surface area of 235.6 mm^2. Sample preparation also involved proper grinding and polishing using metallographic equipment.

Table 2: Chemical composition of the cold rolled duplex stainless steel (wt%)

Grade	Type	Cr	Ni	Mn	Si	P	S	C	N	Mo	Fe
UNS S32205	Standard Duplex	23.64	4.808	1.436	0.496	0.023	<0.100	0.017	0.177	3.245	Balance

3.3.2 Grinding

Metallurgical preparation for the samples was done according to ASTM E3-11(2011). Metallography equipment (Figure 3.3) was used for the grinding of experimental samples to remove surface impurities offering flat, reasonably scratch-free surface with mirror-like reflection for the true observation of the surface. Different grits were available from coarsest to smoother to grind according to their grinding sequence. During grinding, to maximize the grinding paper life and avoid heat generating from the paper, the paper was required to be lubricated with water. The silicon carbide (SiC) paper grinds most materials efficiently at different grits. SiC paper with 240-1200 grit sizes was employed as the grinding for the experiment. Proper grinding was achieved by maintaining flatness and clean surface throughout the preparation process. For final cleaning purposes, the samples were degreased in acetone, rinsed with distilled water and dried with compressed air prior initial weighing for the erosion-corrosion test. Acetone removes any impurity such as corrosion products which could results in rust or any impurity which could not dissolve in water.

Figure 3.2: UNS S32205 work rolled duplex stainless steel

Figure 3.3: SA550 Grinder/Polisher 10 - 12" machine

3.3.3 Etching

The sample immersion or chemical cleaning was done to assist in removing any traces of foreign particles from the surface for metallographic examination. It was also done to further reveal the microstructure of the material by the application of an appropriate etchant. Thorough cleaning and drying of the sample was done prior etching, used well prepared and proper etchant and carefully controlled etching techniques as it is vital during etching application. Reference samples were properly etched using Kroll's reagent (distilled water, Nitric acid and Hydrofluoric acid) for clear microstructural and proper assess the surface.

Table 3: Kroll etchant composition

Kroll Etchant	Distilled Water	Nitric Acid	Hydrofluoric Acid
Quantity	92 ml	6 ml	2 ml

3.4 Sand Particles

For laboratory experimental purposes silica sand was collected from Metal Casting Laboratory (University of Johannesburg), Gauteng, South Africa. Upon receiving the silica sand, sieve analysis for particle size distribution was performed. Different sieve sizes ranging from 500 µm to -75 µm were used to obtain the particle mass in grams in each sieve.

3.5 Underground Mine Water

Underground mine water used for the experiment was collected from Evander gold mine, Mpumalanga, South Africa. It was selected to accomplish the purpose of erosion-corrosion laboratory test on the material of interest. Mine water is usually found in mineral processing such as gold extraction and leaching. Water absorbs chemicals containing different ions which has influence on material mass loss through corrosion process (De la Fuente et al., 2011).

3.6 Gravimetric/Weight Loss Method

Gravimetric method was the initial step to determine the corrosion rate on the sample using RCE test rig. The sample initial mass was weighed on a weighing balance (Figure 3.5) 3 times, for accuracy, then recorded. Each sample was mounted and fully immersed or placed in a beaker filled with measured underground mine water and silica sand to examine the performance of the material to erosion-corrosion conditions that may be experienced in mining industries. After four (4) hour test, each sample was washed with acetone to remove the rust, dirt and moisture and was allowed to dry. Thereafter, the final mass of a dried sample was measured three times, for accuracy, on a weighing balance after the erosion-corrosion test. This was done respectively for each sample to obtain the total mass loss from the environment. The erosion corrosion tests of these alloys under erosion-corrosion tests were conducted at least 3 times and the average results were reported. The formula used to calculate the total mass loss:

TML = Initial mass - Final mass ……………………….. (4)

Samples tend to corrode if kept in sample bags or not preserved after running the test and wear surface can be viewed. Desiccator with a silica gel (drying agent) was used to preserve the samples from corroding further in order to obtain the actual results or true representative of corroded surface from analysis after the erosion-corrosion test. This was done to avoid obtaining the corroded surface which cannot be the representative of the actual surface.

Figure 3.4: Shimadzu AY120 series analytical weighing balance

Figure 3.4 is the weighing balance used to weigh samples and sand particles as part of the experiment before and after the erosion-corrosion test for calculation of mass loss and corrosion rate.

Table 4: Experimental matrix for TML

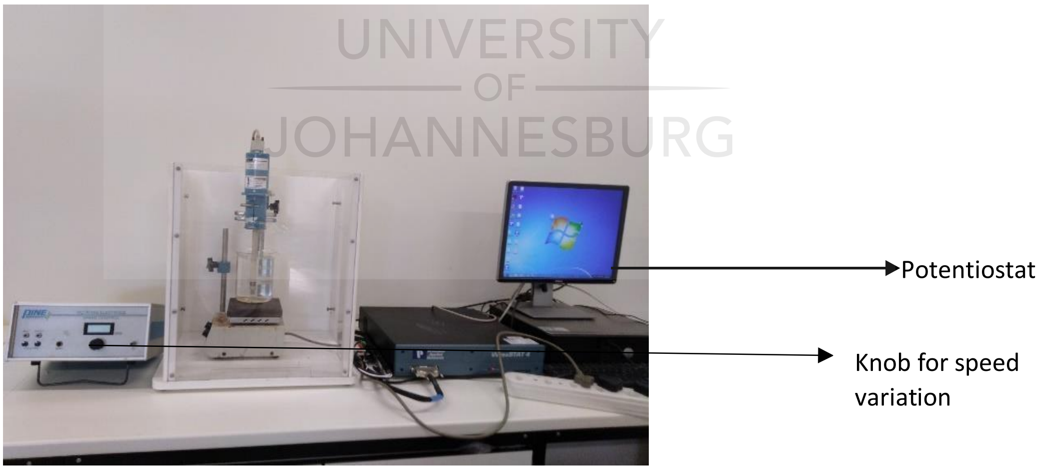
Material	**UNS S32205 cold and hot rolled duplex stainless steel**
Parameters	
Speed (rpm)	1000 1500 2000 2500
Environment	mine water (1000ml)
Sand Particles	Silica sand (5.00g)
Temperature	Room temperature
Time	4 hours (TML)
pH	9.81

3.7 Electrochemical Erosion-Corrosion Testing

The erosion-corrosion tests for the samples were performed using Pine Instrument rotating cylinder electrode with a shaft of 15mm at varied speed of 1000, 1500, 2000 and 2500 rpm. Samples were prepared as explained in 3.3.2 above. The sample which is the working electrode was mounted on the RCE shaft. The reference electrode which is silver/silver chloride, and the graphite counter electrode, which is conductive, were connected to the potentiostat and immersed in the 1000ml mine water beaker. Erosion-corrosion behaviour of each sample was investigated in mine water solutions at the pH of 9.81. For the consistency assurance of the pH, regular checks were made using pen type pH meter.

Electrochemical measurements were carried out at room temperature with a Princeton Applied Research potentiostatic VersaSTAT 4 computer controlled using the Versa Studio software. Electrochemical corrosion testing method was used to determine the corrosion rates of cold and hot rolled duplex stainless steel. Under electrochemical corrosion testing methods open circuit potential and potentiodynamic polarization were used to compare corrosion characterization under subjected environment. Figure 3.5 shows the electrochemical erosioncorrosion testing setup.

The parameter set for OCP was duration time of 3600 seconds to obtain Potential (E) vs Time graph and was plotted for all samples in comparison to determine the corrosion characteristics. Potentiodynamic Polarization was set at an initial potential of -250mV against reference and the final potential of 1600mV. Step time was 4 seconds which gave a scan rate of 0.25mV/s (Aribo et al., 2013) using VersaStudio software. For both OCP and PP graphs were obtained by the immersion of the sample in the solution. The resulting polarisation behaviour was used to identify the corrosion rate. After each test, the solution was replaced together with the solid particles and the samples were then kept in a dessicator.



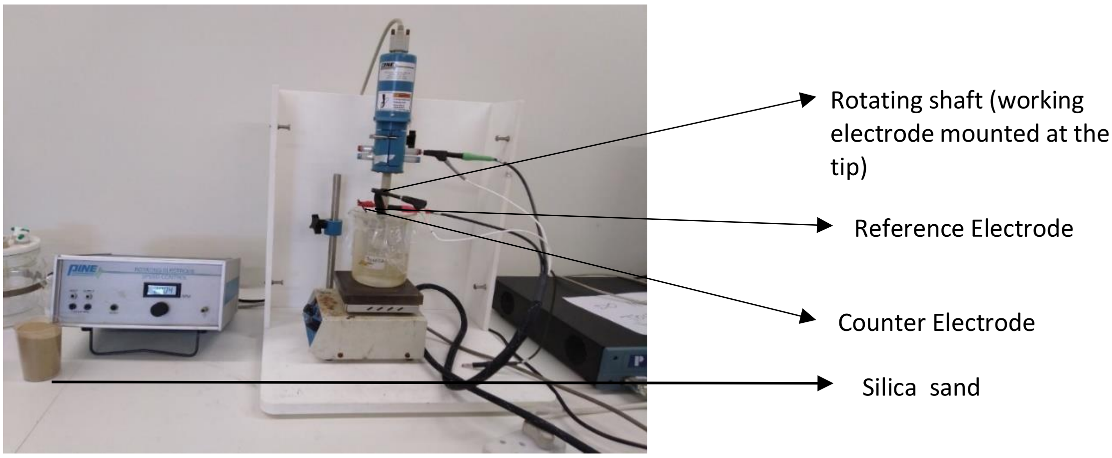
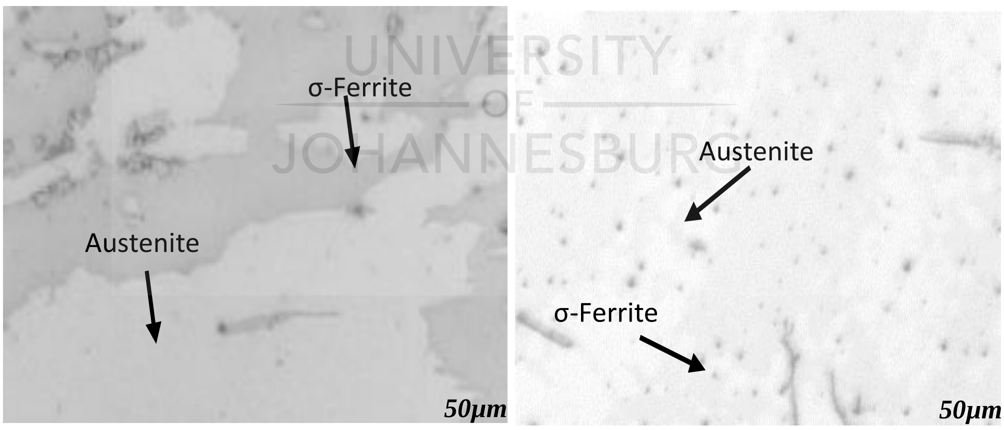


Figure 3.5: Pine Instrument rotating cylinder electrode

3.8 Analysis

3.8.1 Light Optical Microscope

The materials used for the investigation of this study which are cold and hot rolled stainless steel microstructures and their chemical compositions are shown in Figure 3.6 and table 2 respectively.



Cold rolled *Hot rolled*

Figure 3.6: Optical microscope surface microstructure as received stainless steel etched with kroll (92 ml distilled H_20, 6 ml HNO_3 and 2 ml HF)

Sample analysis of etched surface (unexposed samples) and the worn surface samples (exposed samples) after the experiment was carried out for microstructural features to obtain optical micrographs using Zeiss Axio Observer optical microscope. For the interpretation of the changes in properties of the samples, assessment through optical microscope was done. The optical microscope uses visible light and different magnifications to form images through lenses. Samples were examined at appropriate magnifications under the optical microscope as shown in Figure 3.7.

Figure 3.7: Zeiss Axio Observer optical microscope

3.8.2 Scanning Electron Microscope (SEM)

Sample surface morphology and qualitative analyses of reference and corrosive samples were performed using Carl Zeiss Sigma FESEM equipped with an Oxford x-act detector for Energy Dispersive X-ray Spectroscopy (EDS) analysis. Reference samples were properly etched using same reagent for OM samples for clear microstructural. This was done for proper interpretation of erosion-corrosion effect and changes in properties of the samples.

The corrosive samples were analysed using scanning electron microscopy to determine the microstructures of the samples. Zeiss SmartSEM version 5.06 interface software was used to operate the FESEM and INCA suite version 5.04 software was used to analyse the samples for chemistry as shown in Figure 3.8.

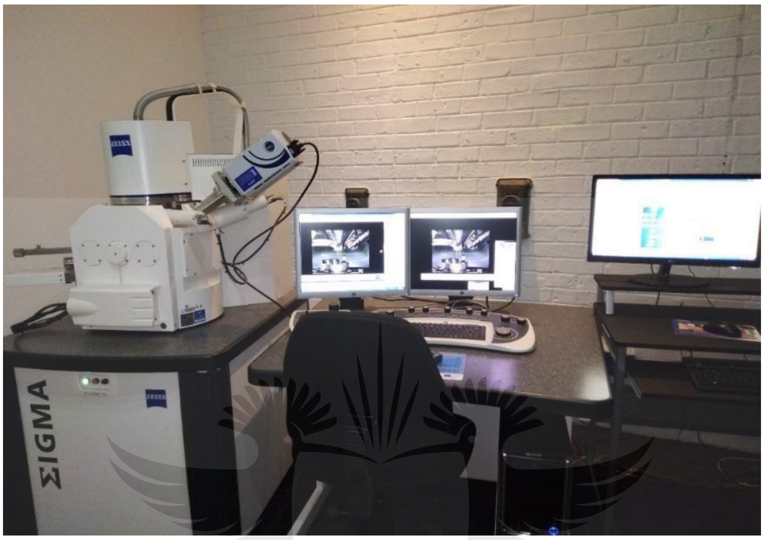


Figure 3.8: Carl Zeiss Sigma Field Emission Scanning Electron Microscope

3.8.3 Microhardness Testing

The microhardness measurements of the materials were conducted using a digital microhardness tester (Future-Tech FM 800) as shown in Figure 3.9 to test the mechanical characteristic, hardness or strength of the materials. Three indents at different locations on the surface of the materials were made at the applied load which was kept at 100 gf for 15s. The diamond shape indention was measured in micrometers (µm).

Figure 3.9: Future-Tech FM 800 microhardness testing machine

CHAPTER FOUR

RESULTS AND DISCUSSION

This chapter presents results obtained from the characterisation of the as-received UNS S32205 duplex stainless steel for both cold and hot rolled materials, corrosion and erosion-corrosion tests. The as-received sample analysis was done to correlate the unexposed surface with corrosion and erosion-corrosion surface degradation. The total mass loss and the surface degradation for the exposed sample performed were to determine the corrosion rate. An electrochemical method was also used to substantiate the total mass loss (TML) method. Surface morphology and hardness of the degraded surfaces were also employed to explain the degradation mechanism.

4.1 As-Received Microstructural Characterisation

Figures 4.1 and 4.2 show both the Optical and SEM micrographs of the as-received duplex stainless steel used for this study. The optical analysis conducted on both alloys revealed that they contain mixture of ferrite and austenite grains as shown in Figure 4.1. Duplex stainless steels are processed by hot rolling or forging and cold rolling followed by suitable recrystallization annealing and quenching to equalize the proportion of the two phases (Reick et al. 1998). The austenite phase assist in offering durability and excellent toughness whereas ferrite offer good ductility and not susceptible to stress corrosion (Charles, 2015). However, the equal amounts of austenite and ferrite in duplex stainless steels are responsible for the improvement of the mechanical properties and corrosion resistance (Tavares et al., 2007). From Fig. 4.1, optical micrograph of duplex stainless steel (cold and hot rolled) show austenite (light grey) and ferrite (dark grey). Also, the observed wavy micrograph after hot rolled has ferrite been disappeared and the microstructure is characterized by thicker bands of austenite and ferrite (Fargas et al. 2009).

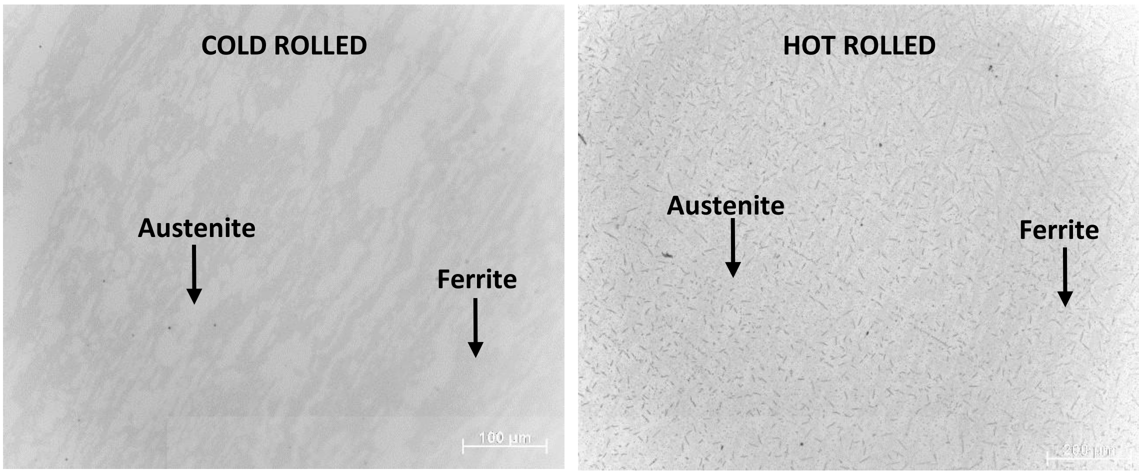


Figure 4.1: Optical micrograph of as-received 2205 duplex stainless steel.

Duplex stainless steels though known with high corrosion resistance are susceptible to pitting corrosion. SEM was employed to obtain the surface morphology of as received samples. The microstructures were clearly revealed as shown in Figure 4.2. In spite the process to manufacture the steel, the microstructure of cold and hot rolled DSS remain the same however the properties differ for both alloys. The existing two phases in the studied cold and hot rolled duplex stainless steel have different corrosion resistances. The ferrite and the austenite phases exhibit different corrosion resistance properties and the weakest phase become vulnerable to the corrosion attack such as pitting (Luo et al., 2012).

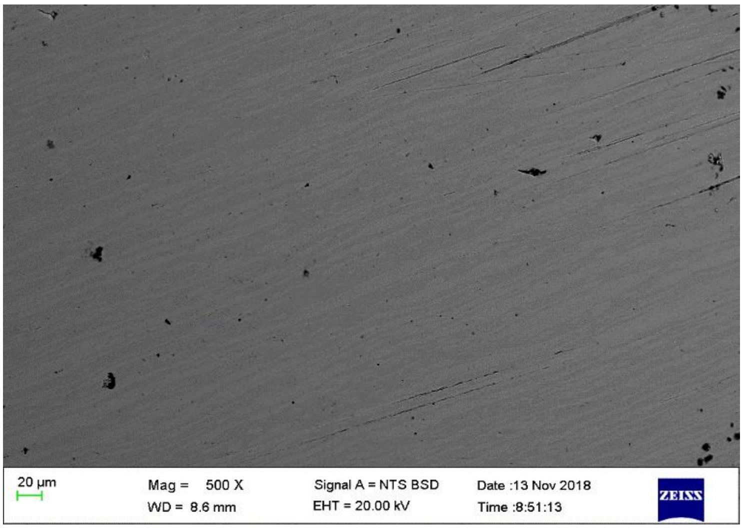


Figure 4.2: SEM micrograph of the as-received 2205 duplex stainless steel

4.1.1 Hardness of as-received duplex stainless-steel samples

The hardness values of the duplex stainless steel were measured using Vickers microhardness tester under an indenter load of 100gf. The hardness value of the cold rolled was 250.96 $HV_{0.1}$ while hot rolled was 221.94 $HV_{0.1}$ as shown in Table 5. Tavares et al. reported that cold rolled hardness reveals high toughness and mechanical properties as compared to hot rolled hardness. Although these alloys depend on equal proportion of austenite and ferrite microstructure for corrosion resistance. The technique used for processing from hot to cold rolling offer great impact to the good properties of the cold rolled steel.

Table 5: As received hardness results

As-received sample	Hardness Value ($HV_{0.1}$)
Cold Rolled	250.96
Hot Rolled	221.94

4.2 Corrosion Tests

4.2.1 Total Mass Loss measurement

Material degradation in the form of total mass loss rates for the alloys was determined by weight loss measurements. However, the flowing of solid particles through magnetic bars/stirrers at the speed of 0 rpm was performed. This allowed the investigation on the effect of particles impingement and aggressive conditions on the material. Environmental and surface compositions interfered with the surface layer causing the reaction taking place as the oxide film dissolves resulting in the mass loss (Table 6). Both material masses decreased however cold rolled still maintained the excellent properties of toughness as compared to hot rolled. The fluid stream caused passive film damage due to the iron combining with the solution and oxygen in a corrosive environment. The encounter caused the material to degrade while an electrochemical reaction took place, causing an increase in corrosion rate. Components such as Cr offer protection at surface material as Guanghong et al., 2010 studies on aggressive conditions, the presence of CrMnN in steels offered superior corrosion resistance.

Table 6: Total mass loss (mg) results of speed at 0 rpm

Samples	**Before EC**	**After EC**
Cold Rolled	4,7229	4,7226
Hot Rolled	4.6046	4,6040

4.2.2 Open Circuit Potential Measurement

Open circuit potential (OCP) measurements were carried out to study and also understand the environmental hydrodynamics on the material surface and susceptibility/tendency of the material to corrode.

The current applied, known as corrosion current density, was used to assess the corroding area induced by the flowing slurry. From Figure 4.3, the OCP generally shift towards positive values for both cold and hot rolled material with curves comparable. A stable OCP values were observed in the materials which display at the initial stage rapid increase in potential from -0.25 V to about -0.15V and then stabilise with time. This indicates that the corrosion resistance of duplex stainless steel is less increased with time and finally reaches a relatively stable OCP value.

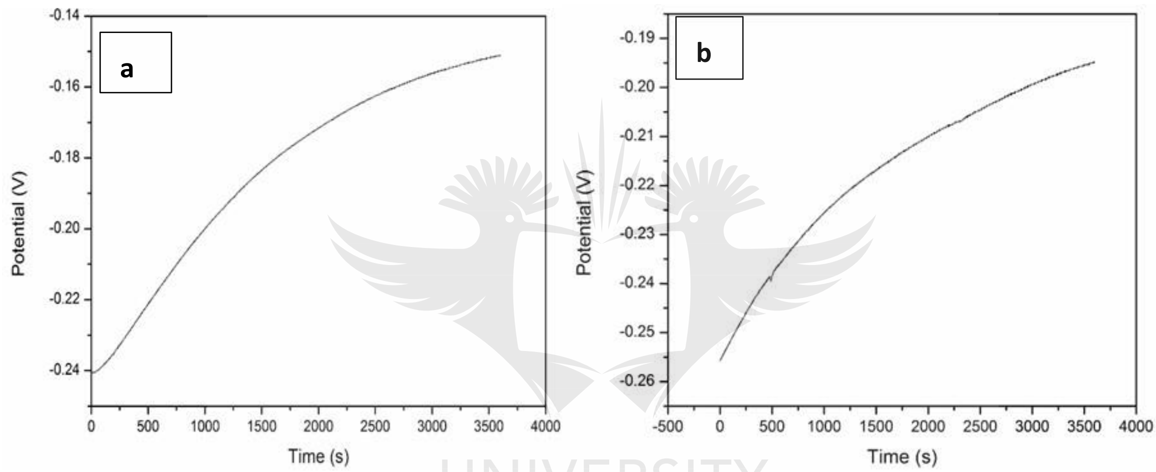


Figure 4.3: Open Circuit Potential (a) cold rolled (b) hot rolled duplex stainless steel at 0 rpm

4.2.3 Potentiodynamic Polarization Measurement

The potentiodynamic polarisation curve obtained for both cold and hot rolled duplex stainless steel after immersion in mine water at room temperature are summarized in Figure 4.4. It was observed that both cold and hot rolled duplex stainless steel displayed similar polarization trends. The material is passive when the potential was under 1.0V. When the potential is higher than 1.0V, pitting occurred in the austenite phase while the ferrite remained passive. Also, when the potential reached to 1V, pitting occurred in both austenite and ferrite phases. Generally, duplex stainless steels are known to be protected by the passive oxide films formed on their surfaces. The protectiveness of passive film depends largely on the Cr, Mo and N contents (Potgieter et al., and Gupta).

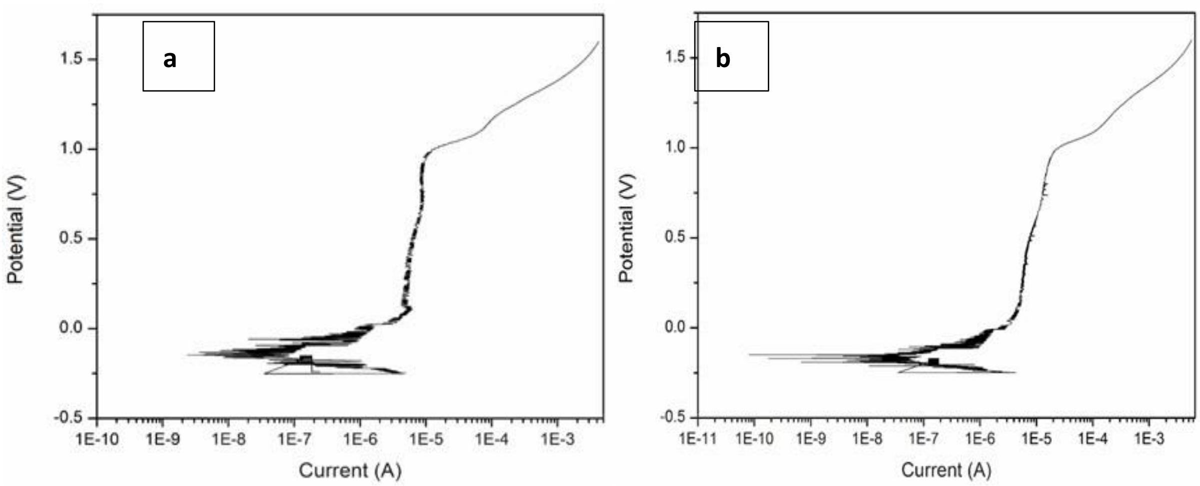


Figure 4.4: Potentiodynamic Polarization curves (a) cold rolled and (b) hot rolled duplex stainless steel at 0 rpm

4.2.4 Effect of Corrosion on the Hardness of Duplex Stainless Steel

The hardness results in Table 7 shows an increase in the hardness value after the corrosion test. Cold rolled show good mechanical properties in spite the environmental conditions. This proves the reliability of the material as compared to hot rolled material.

Table 7: Hardness values ($HV_{0.1}$) of speed at 0 rpm

Samples	**Before EC**	**After EC**
Cold Rolled	250.96	273.10
Hot Rolled	221.94	241.87

4.2.5 Microstructural Characterization after Corrosion Test

The results in Figures 4.5 and 4.6 at 0 rpm reveal the corrosion attack at the surface of the material. This is assumed to be the reaction that exist between iron (Fe) and dissolving oxygen (O_2). This could further explain the particle impingement effect at the initial stage on the surface. The attack depends more on the abrasion or the squeezing process from the particles and the environment. For hot rolled revealing more damage at the surface, it could be due to the chlorine in the environment adding more impact to the attack.

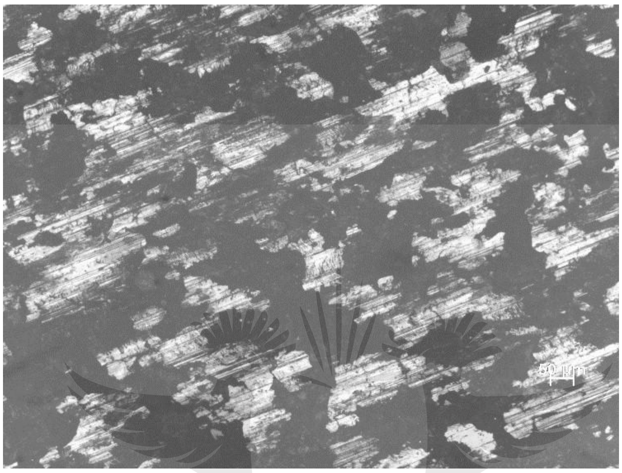


Figure 4.5: Optical microscope image of 2205 duplex stainless steel cold rolled at 0 rpm

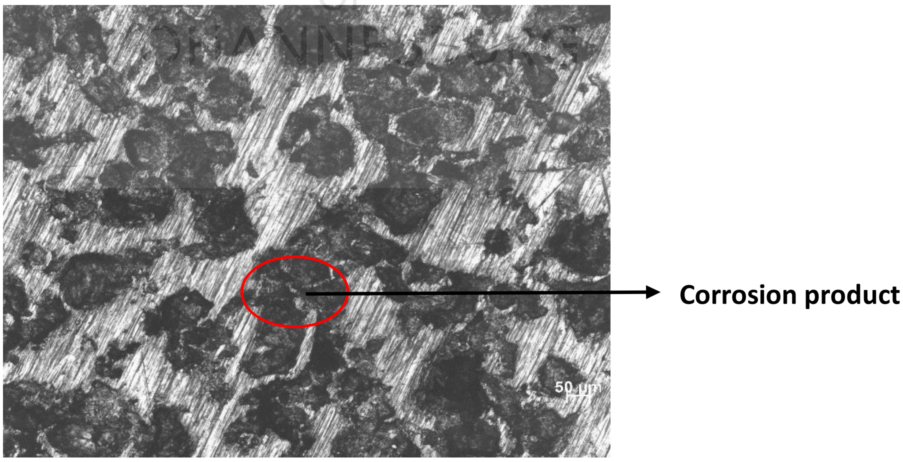


Figure 4.6: Optical microscope image of 2205 duplex stainless steel hot rolled at 0 rpm

Figures 4.7 and 4.8 show SEM results under the experimental conditions. The interaction between the environment and the surface material was investigated on degradation mechanism of corroded cold and hot rolled DSS. Surface degradation investigated under the condition of alkaline environment packed with solid particles was to check the effect of passive layer breakdown or severe pitting for the exposed period. The alloying elements, e,g chromium and thickness of the passive film determine its stability however the stability of the passive layer depends on the environmental composition.

Though DSS is known to exhibit corrosion resistance, wear causes the removal of the protective layer. The solid particle loading improves slurry activities such as mechanical removal of the passive film resulting in less protective to the material surface hence the degradation rate increased. The target material surface become more exposed to the reactions with the environment. Figures 4.7 and 4.8 show passive layer susceptible to corrosion in the form of pitting. The surface also appeared a bit rough due to the impact of solid particles which trigger pitting easily. Depending on the type of flow or the direction in which the fluid is flowing, the system geometry, fluid properties and solid surface roughness are the factors that results in the existence of turbulent flow (Olvera-Martínez et al., 2015).

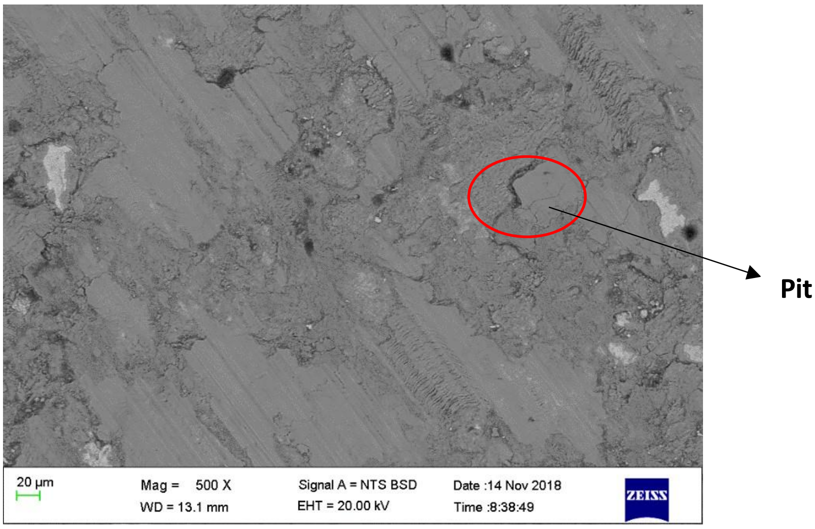


Figure 4.7: SEM micrograph of 2205 cold rolled duplex stainless steel at 0 rpm

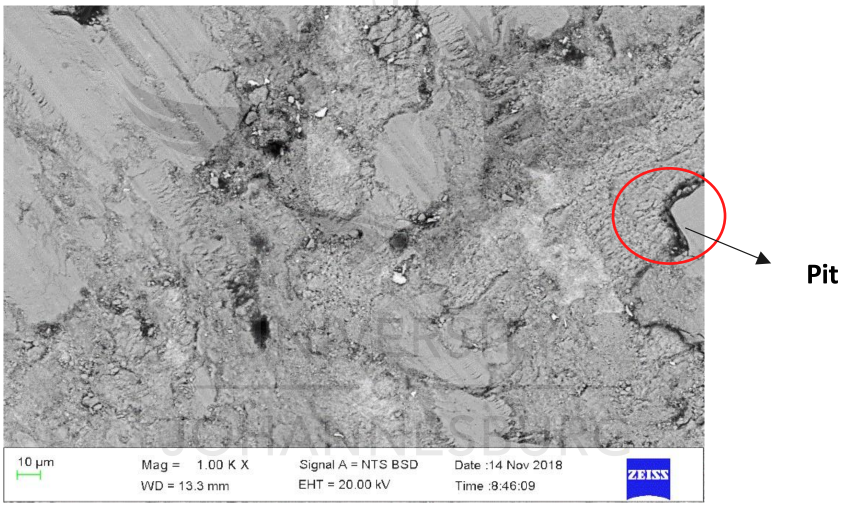


Figure 4.8: SEM micrograph of 2205 hot rolled duplex stainless steel at 0 rpm

4.3 Erosion-Corrosion Tests

4.3.1 Water Analysis

Water analysis was carried out to check the anions such as chloride. In corrosion, the anions are more important because they are aggressive species (negative charge). Chloride ions as a function of pH have an influence on the stability of passive film (Namrata et al, 2014). It is understood that the rate of corrosion may be governed by other minor constituents in the solution, however, more interest was on the major constituents in the solution.

Table 8: Composition of simulated mine water used in this study

Mine water	**Conductivity**	**pH**	**SI Unit**	**Cl^-**	**NO_{3^-}**	**$SO_{4^{2-}}$**	**Ca**	**F^-**	**Mg**	**Na**	**K**
	488 ms/m	9.81	ppm	1355	<0.021	618	242	<0.001	3.08	756	22.90

4.3.2 Particle Size Distribution

PSD was employed to analyze the average mass contributing to the surface impingement during slurry flow. Sieve size of 212 µm contained greater particle mass as compared to all other sieves. The particle has a greater effect on wear due to particle properties such as size and geometry (Woldman et al., 2012). The squeezing process or the abrasion taking place between the environment and the material surface also influence wear mechanism.

Table 9: Particle size distribution results

Sieve size (µm)	500	425	300	212	150	106		75	-75
Particle Mass (g)	22	29	163	164	54	22		9	3

4.3.3 Total Mass Loss Measurements

Mass loss measurements as a function of flow velocity were carried out to determine the rate of material degradation. Time exposed for erosion-corrosion test of 4 hours and sand concentration of 5g/l were kept constant at room temperature during the experiment. The mass loss due to the behavior of passive film caused by the aggravated slurry flow rate take place when the flow is turbulent therefore resulting in erosion-corrosion. The effect of erosioncorrosion on the material resistance was revealed through calculating the mass-loss ratio using the equation below:

$\Delta M' = M_0 - M$ …………………………………………..(5)

M_0 is the material initial weight prior exposure to the corrosive conditions and M is the weight of the material after erosion-corrosion. When the material is subjected to a corrosive condition for over a period of time, degradation process occur whereby both erosion rate and impact velocity affect the material resulting in mass loss.

Results in Figure 4.9 showed that increasing speed resulted in higher material loss for both alloys. However, cold rolled alloy showed better resistance to erosion-corrosion at all the speeds tested. The mass loss through sand impingement and the alkaline environment at 1000 rpm and 2500 rpm speeds showed that hot rolled sample suffered the degradation more with highest material loss of 11.2 mg and 65.2 mg as compared to the cold rolled with the least mass loss of 10 mg and 60 mg respectively. This agrees with the work of Rihan and Nešić., 2006 which explains that the survival of the protective surface film is often affected by the high velocity. The effect of solids particles in a flowing fluid can cause surface film damage through mechanical erosion and material loss mechanism and also induce erosion (Hu and Neville., 2009). Hence the synergy effect from particle concentration and flow velocity resulted in mass loss.

Somani et al., 2009 explained cold rolling as a technique to increase the strength which agrees with the overall results from the graph that shows that material loss by the cold rolled material is less than that of the hot rolled material. The mass change or mass difference after the experiment also serves as erosion-corrosion evidence on the sample surface. To show a good repeatability of the results, error percentage was calculated using the following formula:

$$\text{Error} = measured\ value - actual\ value \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (6)$$

$$\%\ error = \frac{error}{actual\ value} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The percentage error found from the experimental results was 5.7 % which was found fairly low or reasonable.

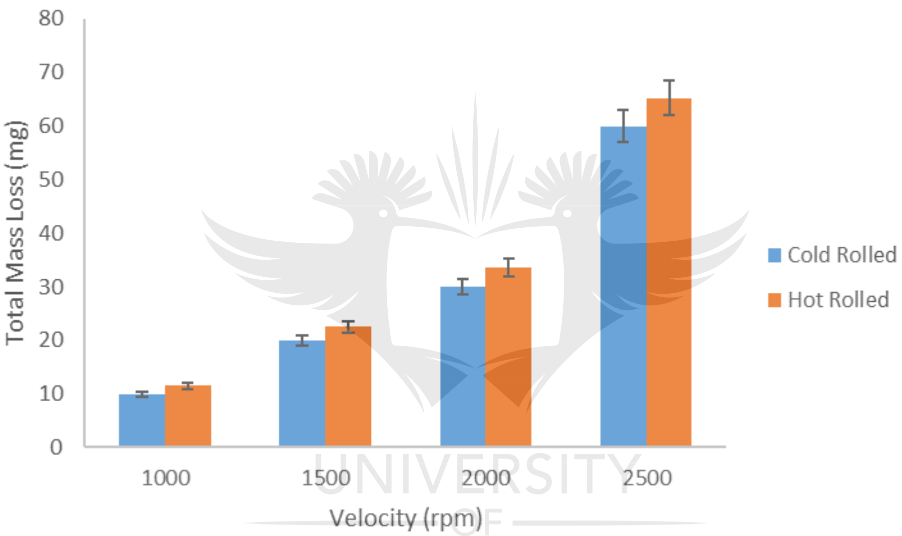


Figure 4.9: Total material loss (TML) for cold and hot rolled UNS S32205 duplex stainless steel

4.3.4 Open Circuit Potential Measurement

To understand erosion-corrosion mechanism, this study in agreement with López et al., 2016, adopted OCP to understand the mechanism behind erosion-corrosion synergism and to also determine the tendency of the material to corrode. Open circuit potential was determined when the system reached a steady state for the duration of 3600 s. According to Hussain & Robinson, 2007, the polarization behavior identifies the potential range for the stability of the passive film. The applied OCP had a potential at which the current was extremely low. Figure 4.10 shows the behavior of the sample for the exposed period. In aggressive conditions the surface material is susceptible to corrode. This is due to dissolved oxygen causing the passive film less stable. The increasing speed tends to increase rate of corrosion and the flow movements at fixed-point resulting in irregular and high frequency pressure, causing the velocity to become constantly changing (Olvera-Martínez et al., 2015). As the speed increased the potential decreased. This resulted in OCP becoming more negative at zero current. When the OCP shifts more to the negative the passive film is destroyed a bit. The increase in speed is known to reveal the susceptibility of the material to corrosion due to poor passivation. The interesting explanation on the behavior of the samples is that the environment was not aggressive enough to breakdown the passive film. The environmental impact was not strong enough to create much interferences which is similar to the study condition done by Hussain and Robinson., 2007 where the condition was sufficient to damage but not remove the layer hence the surface was not as severe.

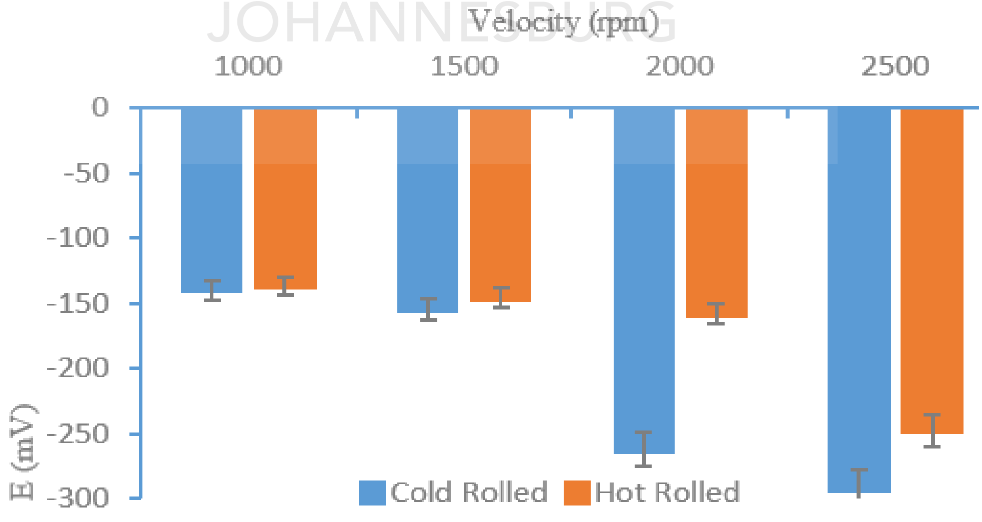


Figure 4.10: Open circuit potential results for UNS S32205 cold and hot rolled in mine water

4.3.5 Potentiodynamic Polarization Measurement

Potentiodynamic polarization (PP) curves assess the behaviour of the material under the synergism of erosion and corrosion. The resistance of duplex stainless steels to erosion–corrosion has been attributed to its ability to repair the passive oxide after it has been damaged under the liquid–solid impingement (M. Jones, R.J. Llewelly and E. Hussain, A. Husain). Tables 10 and 11 show the corrosion potential E_{corr} and corrosion current density i_{corr}, derived from the electrochemical tests using Tafel extrapolation method. The cathodic branches of the polarisation curves for the duplex stainless-steel exhibit current densities that decrease as the applied potential increases. The polarization measurements were performed at a scanning rate of 0.25mV/s and determine the effect of particles on the corrosion rate by applying current. The results revealed an increase in current levels due to sand concentration and increasing velocity. According to Hussain and Robinson, 2007 the increasing speed influence the polarization behavior. Interestingly, the passive film reached a stable stage and passivation process took place in Figure 4.11.

Namrata et al., 2014 stated that higher pH of the solution results in the passivation of the sample. The chloride concentrations in the experimental condition causing instability of the film were not aggressive enough hence re-passivation took place. The anodic current measuring the film formation was a bit low due to the little influence by the particle concentration. Additionally, the anodic regions of the polarization curves for duplex stainless steel display similar pitting potential values which is just after the pseudo-passivation region at about 1.5 V and according to da Silva et al. 2007 stated that a passive film breakdown at 1.6 V was creating a slight/active passive region on the specimen sample surfaces. Corrosion rate was low for both materials which enabled the passivating process (resistance to corrosion layer) to occur as shown in Tables 10 and 11. Therefore the formation of a passive layer or film on the surface provided high corrosion resistance reducing the electrochemical reactions on the surface.

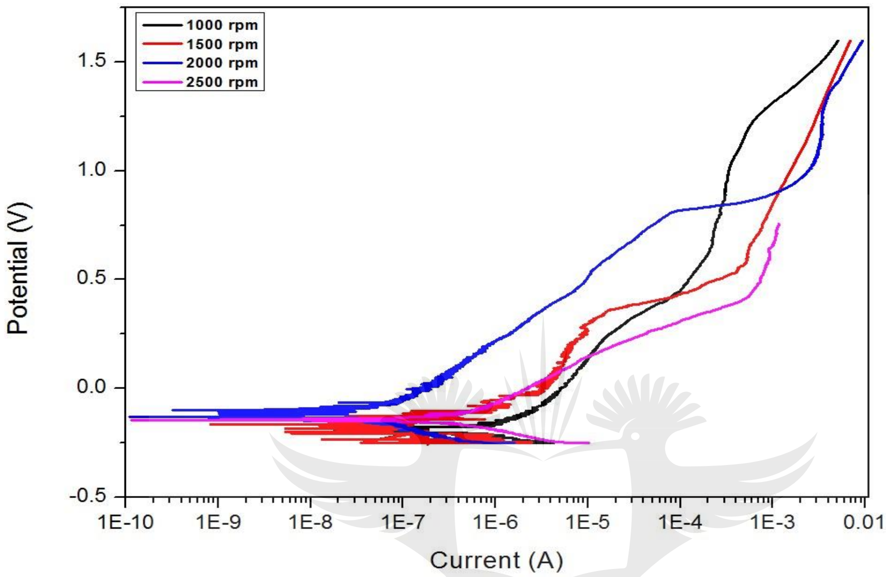


Figure 4.11: Potentiodynamic polarization curves for UNS S32205 duplex stainless steel (cold rolled) in mine water.

Table 10: Cold rolled corrosion rate

Velocity (rpm)	I_{corr} (nA)	E_{corr} (mV)	Corrosion Rate (mpy)	I_p (nA)
1000	54.755	-156.726	0.0091329	0.2893
1500	311.441	-165.845	0.051946	0.493
2000	451.289	-176.662	0.075272	0.509
2500	740.888	-207.639	0.12358	0.552

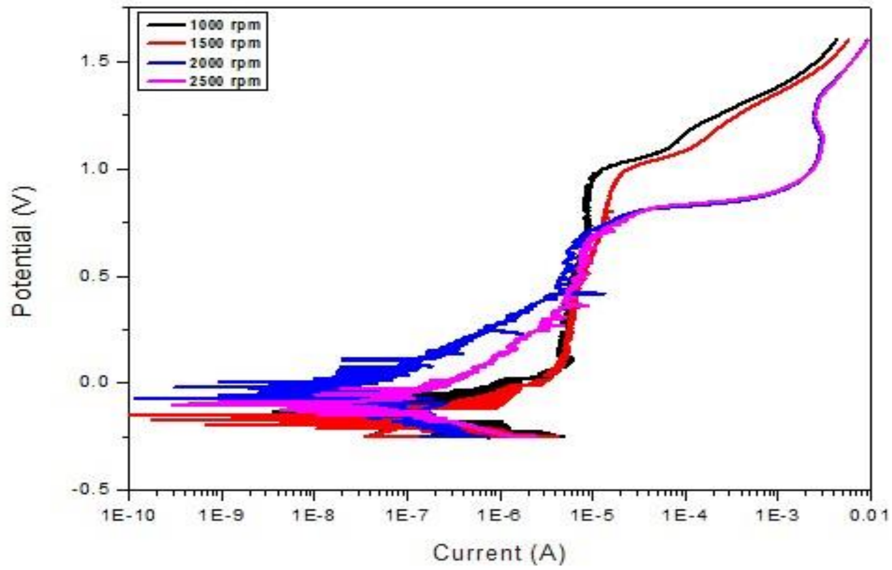


Figure 4.12: Potentiodynamic polarization curves for UNS S32205 duplex stainless steel (hot rolled) in mine water.

Table 11: Hot rolled corrosion rate

Velocity (rpm)	I_{corr} (nA)	E_{corr} (mV)	Corrosion Rate (mpy)	I_p (nA)
1000	44.647	-64.715	0.0074469	0.247
1500	266.805	-110.72	0.044501	0.299
2000	354.413	-171.448	0.059114	0.4715
2500	556.074	-204.266	0.07945	0.529

4.3.6 Effect of Corrosion on Hardness of the Alloy

Aggressive environments are reported as the most common cause of severe failure in various materials (Verma and Taiwade, 2017) and DSS are known for their superior resistance to aggressive environments. Somani et al., 2009 explained cold rolling as a technique, applied industrially to increase the material strength which agrees with

Pramanik et al., 2014 that cold rolling improve the strength and hardness of the material. Table 12 and Figure 4.13 is in agreement with these researchers on cold rolling strength as compared to hot rolled. The rotating corrosive solution and the silica sand simulated erosion-corrosion slurry conditions. A chromium-rich metal has the ability to resist the external interferences taking place in contact with the environment. Aribo et al., 2013 reported that impingement by sand particle on duplex and austenitic stainless steels led to increase hardness and hence better resistance to erosioncorrosion. The increase in hardness from the obtained results is attributed to the increase in speed which corroborated this conclusions. It is noteworthy that the trend of hardness increase which is the same for cold and hot rolled validate that there is truly an increase in hardness with speed. The total kinetic energy of particles impacting the surface in one second according to Hussain and Robinson, 2007 is as follows:

$KE = (Nm_{av}V^2)/2$ …………………………………….. (8)

N = Number of impacts per seconds, m_{av} = Average mass of a sand particle,

V = Particle velocity

Kinetic energy being generally related to the motion, in this case of the slurry, at a certain velocity is considered as a parameter that contribute to the material degradation. Sand particle has an impact on the passive film through the effect of kinetic energy which involves the rate at which the particle travels due to the velocity applied. The higher speed is directly proportional to the higher kinetic energy which then results in an increase in hardness. The results are consistent as the synergy of erosion-corrosion is greater than corrosion occurring individually (Aribo, 2014).

Table 12: Hardness results

Sample Material (After EC)				
Speed (rpm)	1000	1500	2000	2500
Hardness Value (Vickers HV)				
Cold Rolled	284.03	305.64	316.89	338.52
Hot Rolled	245.08	270.18	278.18	303.18

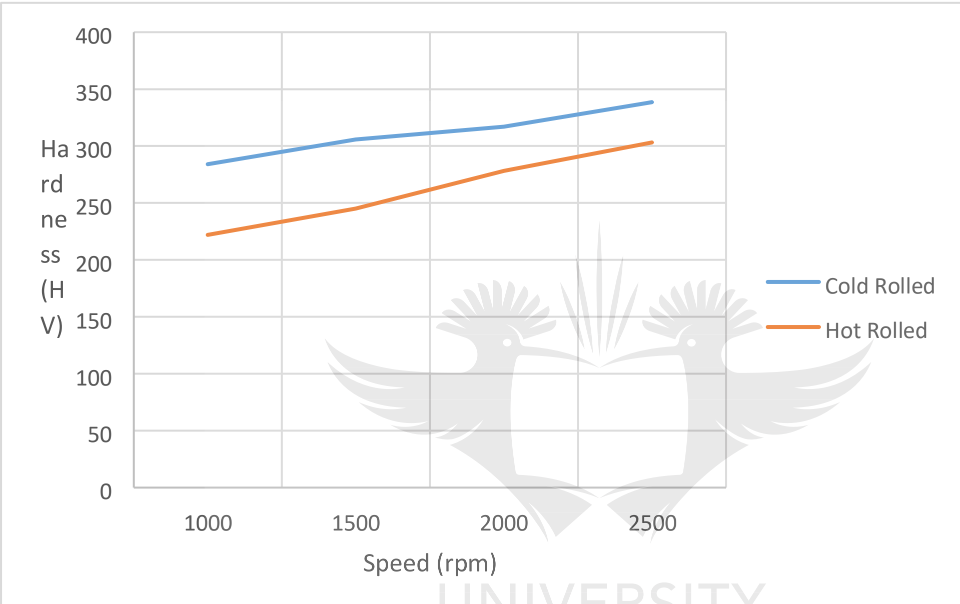


Figure 4.13: Graph showing the relationship between hardness and erosion-corrosion speed

4.3.7 Microstructural Characteristics of the Eroded Alloys

The test parameters set allowed observation of possible erosion-corrosion performance of the material in mining industries as compared to other different material's performance. The parameters of interest affecting the behaviour of the material was solid particles and aggressiveness of the environment.

Figure 4.14: Optical micrograph of 2205 hot rolled duplex stainless steel at 1500 rpm after erosion-corrosion

Figure 4.15: Optical micrograph of 2205 hot rolled duplex stainless steel at 2500 rpm after erosion-corrosion.

Since the particles differ in shape and geometry the abrasion severity is seen at 2000 and 2500 rpm against the surface causing the passive film damage severity as the speed increased. The results represent the effect that the particles has on the surface resulting in wear mechanism grooving as shown in Figure 4.16. The grooving was seen severe as the speed increased to 2500 rpm as shown in Figure 4.17 (circled). The mechanical interactions displayed greater influence as the wear grew deeper on the surface. These results display the relationship the wear rate has with the grooving due to an increase in speed restricting the passivation process to occur. The combination of particles properties and environmental composition restrict the protective layer due to the severity depth generated as a results of wear.

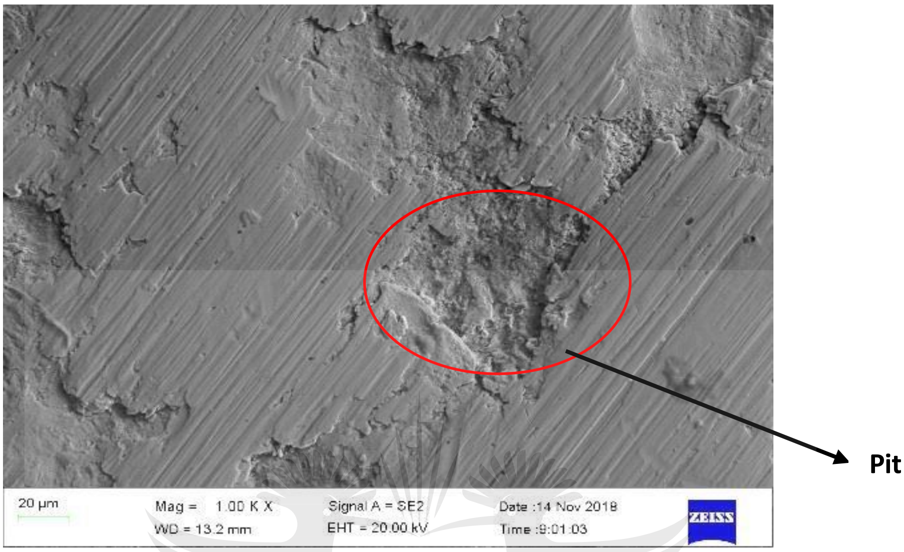


Figure 4.16: SEM micrograph of 2205 hot rolled duplex stainless steel at 2000 rpm after erosion-corrosion

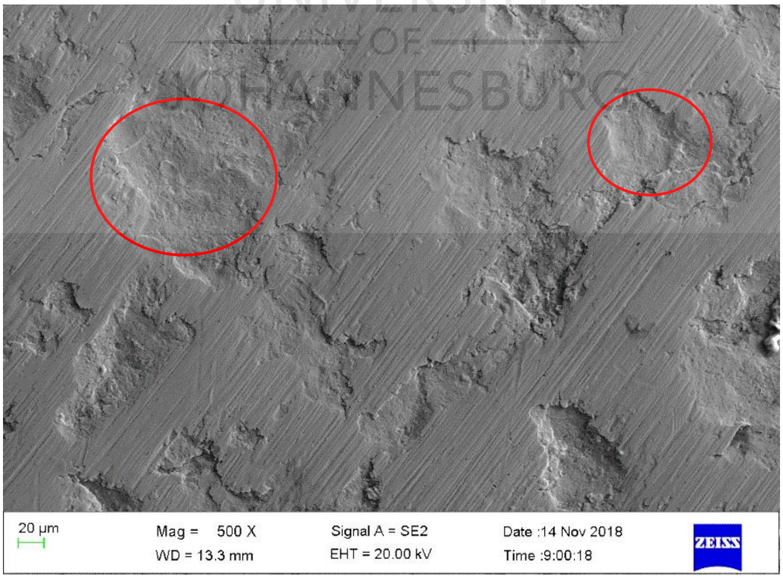


Figure 4.17: SEM micrograph of 2205 hot rolled duplex stainless steel at 2500 rpm after erosion-corrosion

The SEM micrographs of the erosion-corrosion mechanism with the corresponding surface appearance seem slightly different. Figure 4.11 and Figure 4.12 show the minimal evidence of pitting which increased with the increase in speed of 2500 rpm. This is supported by El-Egamy & Badaway, 2004 stating that the unfavourable environmental conditions initiate the breakdown of passivity causing primary failure on the sample surface through pitting. The tendency for passivation and the formation of surface layer or the passive film on the material at the speed of 2000 rpm as compared to the higher speed of 2500 rpm experienced some difficulty against the environmental condition. Corrosion rate proportion to the speed. Wood et al., 2013 investigated on the surface material response of a stainless 316 alloy subjected to erosion and erosion–corrosion. Mass loss rate resulted under both subjected conditions. The synergy rate was higher compared to pure erosion. Although chloride causes pitting but under this condition, the effect of chloride will be the same for all the speed (1000, 1500,2000 & 2500 rpm). Erosion dominated on the synergy of erosion-corrosion process revealing the micrograph features that are in conformity with the damage caused by the particles.

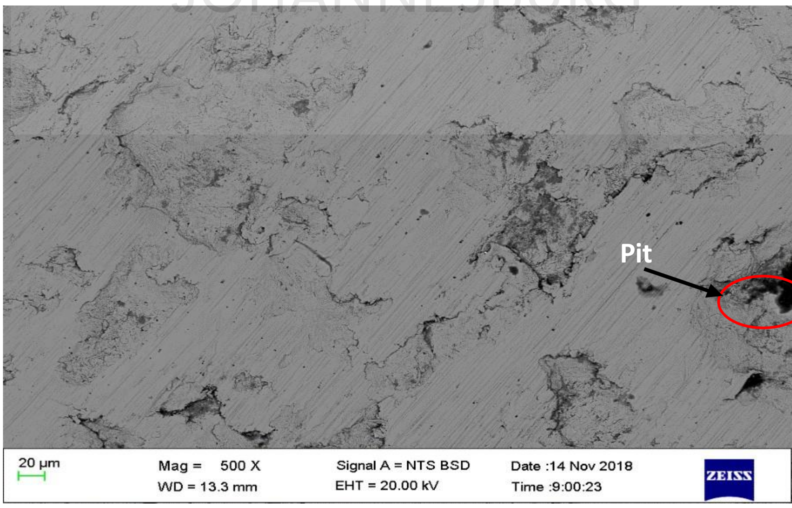


Figure 4.18: SEM micrograph of 2205 hot rolled duplex stainless steel at 2000 rpm after erosion-corrosion

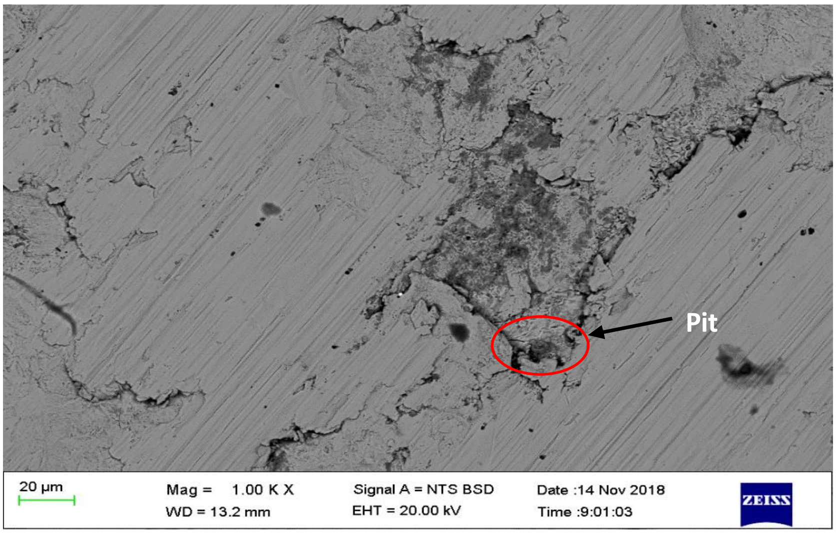


Figure 4.19: SEM micrograph of 2205 hot rolled duplex stainless steel at 2500 rpm after erosion-corrosion

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Erosion–corrosion synergism results in high metal wastage rates. This is due to the hydrodynamic parameters impacting on the material when exposed to the corrosive environment. The presence of solid particles affects the microstructure by impinging against the surface material mechanically removing the passive film. Turbulent flow and impact velocity also play a crucial role in the corrosion process. The erosion-corrosion of UNS S32205 cold and hot duplex stainless steel by experimental conditions of alkaline environment together with solid particles has been conducted.

Mechanical impact occurring during the flow of the solution on the material surface was sufficient enough to cause mass loss. However, the slurry was not aggressive enough to cause severe damage as the passive film seems to repassivate. The low kinetic energy the particles possessed or the pure erosion was not sufficient. Similar passive film behavior showed in the analysis. It was expected to observe the wear mechanism grooving especially at a high speed of 2500 rpm. The wear process is due to the particle properties traveling and impinging against the surface material. It is clear that introducing particles to aggressive conditions accelerates the wear rate. Hence, the trend was not surprising as the velocity was increasing resulting in the layer vulnerable to the environmental conditions. Abrasive wear could be related to the grooving taking place on the material. An increase in velocity increased the hardness of both materials which prove better resistance to erosion-corrosion. The polarization behavior was influenced by an increasing speed and as a result the depassivation process associated with high corrosion rate and more negative potentials.

5.2 Recommendations

From the laboratory method used to test the erosion-corrosion behavior of UNS S32205 cold and hot rolled duplex stainless steel in mine water using the RCE, it was recommended that

- Extended time exposure of the tested steels in pure alkaline environment with solid particle be considered to reveal the period it might take for the breakdown of the passive film
- Sand concentration should be taken into consideration to check the concentration that might have greater impact against pure erosion and pure corrosion to occur

5.3 References

Aribo, S., 2014. Corrosion and erosion-corrosion behaviour of lean duplex stainless steels in marine and oilfield environments (Doctoral dissertation, University of Leeds).

Aribo, S., Barker, R., Hu, X. and Neville, A., 2013. Erosion-corrosion behavior of lean duplex stainless steels in 3.5% NaCl solution. *Wear,* 302(1-2), pp. 1602-1608.

Baboian, R. (2005). Corrosion tests and standards: application and interpretation, ASTM international.

Bermúdez, M.D., Carrión, F.J., Martínez-Nicolás, G. and López, R., 2005. Erosion–corrosion of stainless steels, titanium, tantalum and zirconium. *Wear*, *258*(1-4), pp.693-700.

Bokati, K.S., Dehghanian, C. and Yari, S., 2017. Corrosion inhibition of copper, mild steel and galvanically coupled copper-mild steel in artificial sea water in presence of 1H-benzotriazole, sodium molybdate and sodium phosphate. *Corrosion Science,* 126: 272-285

Capendale, A.E., 1985. The influence of water composition on the pitting behaviour of stainless steel (Doctoral dissertation, University of Cape Town).

Carter, A.M.F., 1986. Erosion, corrosion, and abrasion of material-handling systems in the mining industry. *Journal of the Southern African Institute of Mining and Metallurgy*, 86(7), pp.235-242.

Center, M.P., 2000. Cyanide leach mining packet. Washington, DC: Mineral Policy Center. Retrieved October, 3, p.2007.

Charles, J., 2015. Duplex families and applications: a review Part 1: From Duplex Pioneers up to 1991. *Stainless Steel World*, p.1.

De la Fuente, D., Díaz, I., Simancas, J., Chico, B. and Morcillo, M., 2011. Long-term atmospheric corrosion of mild steel. *Corrosion Science,* 53(2), pp.604-617.

De Waard, C., Lotz, U. and Milliams, D.E., 1991. Predictive model for CO2 corrosion engineering in wet natural gas pipelines. *Corrosion*, 47(12), pp.976-985.

Della Rovere, C.A., Aquino, J.M., Ribeiro, C.R., Silva, R., Alcântara, N.G. and Kuri, S.E., 2015. Corrosion behavior of radial friction welded supermartensitic stainless steel pipes. *Materials & Design* (1980-2015), 65, pp.318-327.

El-Egamy, S.S. and Badaway, W.A., 2004. Passivity and passivity breakdown of 304 stainless steel in alkaline sodium sulphate solutions. *Journal of Applied Electrochemistry*, *34*(11), pp.1153-1158.

Fargas, G., Anglada, M. and Mateo, A., 2009. Effect of the annealing temperature on the mechanical properties, formability and corrosion resistance of hot-rolled duplex stainless steel. *Journal of materials processing technology*, 209(4), pp.1770-1782.

Gall, F., 2013. The Corrosion of Centrifugal Pumps in Aqueous Environments.

Giourntas, L., Hodgkiess, T. and Galloway, A.M., 2015. Comparative study of erosion–corrosion performance on a range of stainless steels. *Wear*, 332, pp.1051-1058.

Guanghong, Z., Hongyan, D., Yue, Z. and Nianlian, L., 2010. Corrosion–erosion wear behaviors of 13Cr24Mn0. 44N stainless steel in saline–sand slurry. *Tribology International*, 43(5-6), pp.891-896.

Hango, S.I., Chown, L.H., Van der Merwe, J.W., Kavishe, F.P. and Cornish, L.A., 2014. Corrosion of selected hard facing materials exposed to mine water.

http://www2.ucdsb.on.ca/tiss/stretton/chem2/corrosion.html. [Accessed 12/02/2019]

Hossain, M.S.J., 2017. Optimization of a steel pipe manufacturing system to improve overall effectiveness.

Hu, X. and Neville, A., 2009. CO2 erosion–corrosion of pipeline steel (API X65) in oil and gas conditions—A systematic approach. *Wear*, 267(11), pp.2027-2032.

Hu, X. and Neville, A., 2005. The electrochemical response of stainless steels in liquid–solid impingement. *Wear*, 258(1), pp.641-648.

Hussain, E.A.M. and Robinson, M.J., 2007. Erosion–corrosion of 2205 duplex stainless steel in flowing seawater containing sand particles. *Corrosion Science*, 49(4), pp.1737-1754.

Ige, O.O., Aribo, S., Obadele, B.A., Langa, T., Oluwasegun, K.M., Shongwe, M.B. and Olubambi, P.A., 2017. Erosion–corrosion behaviour of spark plasma sintered WC-12Co in aggressive media. International Journal of Refractory Metals and Hard Materials, 66, pp.3643. Islam, M.A. and Farhat, Z., 2017. Erosion-corrosion mechanism and comparison of erosion-corrosion performance of API steels. *Wear*, 376, pp.533-541.

Ige, O.O., Aribo, S., Obadele, B.A., Langa, T. and Olubambi, P.A., 2017. Erosion-corrosion characteristics of spark plasma sintered pure nickel in simulated mine water. *Tribology International*, 109, pp.441-446.

Islam, M.A. and Farhat, Z., 2017. Erosion-corrosion mechanism and comparison of erosioncorrosion performance of API steels. *Wear*, 376, pp.533-541.

Iversen, A. and Leffler, B., 2010. Aqueous corrosion of stainless steels.

Jiang, R., Wang, Y., Wen, X., Chen, C. and Zhao, J., 2017. Effect of time on the characteristics of passive film formed on stainless steel. *Applied Surface Science*, 412, pp.214-222.

Junior, M.W., Reis, J.M.L. and da Costa Mattos, H.S., 2017. Polymer-based composite repair system for severely corroded circumferential welds in steel pipes. *Engineering Failure Analysis*, 81, pp.135-144.

Kabeel, A.E. & Abdelgaied, M. 2013, Study on the effect of alumina nano-fluid on sharp-edge orifice flow characteristics in both cavitations and non-cavitations turbulent flow regimes.

Khayatan, N., Ghasemi, H.M. and Abedini, M., 2017. Synergistic erosion-corrosion behavior of commercially pure titanium at various impingement angles. *Wear*, 380, pp.154-162.

Kimura, T., Tokoo, N., Ogata, M., Nojima, M. and Kuwabara, K., 2017. Chromium-Based Duplex Alloy for Wear and Corrosion Resistant Cladding. *MATERIALS TRANSACTIONS*, 58(4), pp.619-622.

Kuruvila, R., Kumaran, S.T., Khan, M.A. and Uthayakumar, M., 2018. A brief review on the erosion-corrosion behavior of engineering materials. Corrosion Reviews.

Liu, Z., Gao, X., Du, L., Li, J., Li, P., Yu, C., Misra, R.D.K. and Wang, Y., 2017. Comparison of corrosion behaviour of low-alloy pipeline steel exposed to H 2 S/CO 2-saturated brine and vapour-saturated H 2 S/CO 2 environments. *Electrochimica Acta*, 232, pp.528-541.

Li, G.Y. and Lei, M.K., 2017. Microstructure and Properties of Plasma Source Nitrided AISI 316 Austenitic Stainless Steel. *Journal of Materials Engineering and Performance*, 26(1), pp.418-423.

Long, Y., Li, D.G. and Chen, D.R., 2017. Influence of square wave anodization on the electronic properties and structures of the passive films on Ti in sulfuric acid solution. *Applied Surface Science*, 425, pp.83-94.

López, D.M., Alonso Falleiros, N. and Tschiptschin, A.P., 2016. Use of Electrochemical Tests for Assessment of the Effect of Erosive Particle Size on the Erosion-Corrosion Behaviour of AISI 304L Austenitic Stainless Steel. *Materials Research*, 19(2), pp.451-458.

Luo, H., Dong, C.F., Li, X.G. and Xiao, K., 2012. The electrochemical behavior of 2205 duplex stainless steel in alkaline solutions with different pH in the presence of chloride. *Electrochimica Acta*, 64, pp. 211-220.

Luo, H., Li, Z., Chen, Y.H., Ponge, D., Rohwerder, M. and Raabe, D., 2017. Hydrogen effects on microstructural evolution and passive film characteristics of a duplex stainless steel. *Electrochemistry Communications*, 79, pp.28-32.

Matsumura, M., 2012. Erosion-Corrosion: An introduction to flow induced macro-cell corrosion. Bentham Science Publishers.

Mohammadi, F., 2011. Erosion-corrosion of 304 stainless steel. (Doctoral dissertation, University of Alberta).

Moura, V.S., Lima, L.D., Pardal, J.M., Kina, A.Y., Corte, R.R.A. and Tavares, S.S.M., 2008. Influence of microstructure on the corrosion resistance of the duplex stainless steel UNS S31803. *Materials Characterization*, 59(8), pp.1127-1132.

More, S.R., Bhatt, D.V. and Menghani, J.V., 2017. Recent Research Status on Erosion Wear– An Overview. *Materials Today: Proceedings*, 4(2), pp.257-266.

Myles, K., 1995, Corrosion Control: Principles and Practice, K. Myles and Associates Publishers, Northcliff.

Naz, M.Y., Sulaiman, S.A., Shukrullah, S., Ghaffar, A., Ibrahim, K.A. and AbdEl-Salam, N.M., 2017. Development of erosion-corrosion mechanisms for the study of steel surface behavior in a sand slurry. *Measurement*, 106, pp.203-210.

Nelwalani, N.B., 2014. Evaluation of Erosion-corrosion on Ruthenium Enriched Hardmetal Coatings (Doctoral dissertation, University of Johannesburg).

Neville, A. and Hu, X., 2001. Mechanical and electrochemical interactions during liquid–solid impingement on high-alloy stainless steels. *Wear*, 251(1-12), pp.1284-1294.

Neville, A. and Wang, C., 2009. Erosion–corrosion of engineering steels—Can it be managed by use of chemicals? *Wear*, 267(11), pp.2018-2026.

Neville, A., Hodgkiess, T. and Dallas, J.T., 1995. A study of the erosion-corrosion behaviour of engineering steels for marine pumping applications. *Wear*, 186, pp.497-507.

Okonkwo, P.C. and Mohamed, A.M., 2014. Erosion-corrosion in oil and gas industry: a review. Int. J. Metall. *Mater. Sci. Eng*, 4(3), pp.7-28.

Okonkwo, P.C., Shakoor, R.A., Zagho, M.M. and Mohamed, A.M.A., 2016. Erosion Behaviour of API X100 Pipeline Steel at Various Impact Angles and Particle Speeds. *Metals*, 6(10), p.232.

Onyebuchi, V.E., Kolios, A., Hanak, D.P., Biliyok, C. and Manovic, V., 2017. A systematic review of key challenges of CO2 transport via pipelines. Renewable and Sustainable Energy Reviews.

Örnek, C. and Engelberg, D.L., 2015. SKPFM measured Volta potential correlated with strain localisation in microstructure to understand corrosion susceptibility of cold-rolled grade 2205 duplex stainless steel. *Corrosion Science*, 99, pp.164-171.

Pandya, D.A., Dennis, B.H. and Russell, R.D., 2017. A computational fluid dynamics based artificial neural network model to predict solid particle erosion. *Wear*, 378, pp.198-210.

Peng, W. and Cao, X., 2016. Numerical simulation of solid particle erosion in pipe bends for liquid–solid flow. *Powder Technology*, 294, pp.266-279.

Pramanik, S., Bera, S. and Ghosh, S.K., 2014. Influence of cold rolling on microstructural evolution in 2205 duplex stainless steel. *steel research international*, 85(5), pp.776-783.

Qiu, J.H., 2002. Passivity and its breakdown on stainless steels and alloys. Surface and Interface Analysis: An International Journal devoted to the development and application of techniques for the analysis of surfaces, interfaces and thin films, 33(10-11), pp.830-833.

Rajahram, S.S., Harvey, T.J. and Wood, R.J.K., 2011. Electrochemical investigation of erosion–corrosion using a slurry pot erosion tester. *Tribology International*, 44(3), pp.232-240.

Rajahram, S.S., 2010. Erosion-corrosion mechanisms of stainless steel UNS S31603 (Doctoral dissertation, University of Southampton).

Rajahram, S.S., Harvey, T.J. and Wood, R.J.K., 2009. Erosion–corrosion resistance of engineering materials in various test conditions. *Wear*, 267(1), pp.244-254.

Rihan, R.O. and Nešić, S., 2006. Erosion–corrosion of mild steel in hot caustic. Part I: NaOH solution. *Corrosion Science,* 48(9), pp.2633-2659.

Shirazi, S.A., Shadley, J.R., McLaury, B.S. and Rybicki, E.F., 1995. A procedure to predict solid particle erosion in elbows and tees. *Journal of Pressure Vessel Technology*, 117(1), pp.45-52.

Shockley, J.M., Horton, D.J. and Wahl, K.J., 2017. Effect of aging of 2507 super duplex stainless steel on sliding tribocorrosion in chloride solution. *Wear*, 380, pp.251-259.

Shrestha, S.K., 2000. Corrosion and erosion-corrosion of High Velocity Oxy-Fuel (HVOF) sprayed NiCrSiB coatings (Doctoral dissertation, University of Glasgow).

Tański, T., Brytan, Z. and Labisz, K., 2014. Fatigue behaviour of sintered duplex stainless steel. *Procedia Engineering*, 74, pp.421-428.

Tavares, S.S.M., Silva, V.G., Pardal, J.M. and Corte, J.S., 2013. Investigation of stress corrosion cracks in a UNS S32750 superduplex stainless steel. *Engineering Failure Analysis*, 35, pp.88-94.

Tavares, S.S.M., Pardal, J.M., Lima, L.D., Bastos, I.N., Nascimento, A.M. and De Souza, J.A., 2007. Characterization of microstructure, chemical composition, corrosion resistance and toughness of a multipass weld joint of superduplex stainless steel UNS S32750. *Materials Characterization*, *58*(7), pp.610-616.

Verma, J. and Taiwade, R.V., 2017. Effect of welding processes and conditions on the microstructure, mechanical properties and corrosion resistance of duplex stainless steel weldments—A review. *Journal of Manufacturing Processes*, 25, pp.134-152.

Wang, D., Zhu, Z., He, B., Ge, Y. and Zhu, D., 2017. Effect of the breakdown time of a passive film on the electrochemical machining of rotating cylindrical electrode in NaNO 3 solution. *Journal of Materials Processing Technology*, 239, pp.251-257.

Wang, L., Xing, Y., Liu, Z., Zhang, D., Du, C. and Li, X., 2016. Erosion–corrosion behavior of 2205 duplex stainless steel in wet gas environments. Journal of Natural Gas Science and Engineering, 35, pp.928-934.

Winde, F., Kaiser, F. and Erasmus, E., 2017. Exploring the use of deep level gold mines in South Africa for underground pumped hydroelectric energy storage schemes. *Renewable and Sustainable Energy Reviews*, 78, pp.668-682.

Woldman, M., van der Heide, E., Schipper, D.J., Tinga, T. and Masen, M.A., 2012. Investigating the influence of sand particle properties on abrasive wear behaviour. *Wear*, *294*, pp.419-426.

Wood, R.J.K., Walker, J.C., Harvey, T.J., Wang, S. and Rajahram, S.S., 2013. Influence of microstructure on the erosion and erosion–corrosion characteristics of 316 stainless steel. *Wear*, 306(1), pp.254-262.

Zheng, Y.G., Yao, Z.M. and Ke, W., 2000. Erosion–corrosion resistant alloy development for aggressive slurry flows. *Materials Letters*, 46(6), pp.362-368.